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Accurate determination of the cell dimensions of magnetite.

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Summary. An analysed magnetite from Bisperg, Säter, Dalecarlia, Sweden, gave the formula $Fe^{2+}_{1\cdot024}Mg^{2+}_{0\cdot010}Fe^{3+}_{1\cdot984}O_{4\cdot000}$, which corresponds closely to the ideal composition. A precise determination of the cell dimensions gave a 8·3963 ± 0·0005 Å. at 18° C. Gentle heating of the powdered magnetite in evacuated silica glass tubes, before X-ray examination, resulted in sharply defined lines with high Bragg angles; an improvement which enabled precision data to be obtained. Four other new analyses of magnetites are also given and their lattice parameters are determined in the same way and are found to range from 8·3960 Å. to 8·3970 Å. The Bisperg magnetite being the purest sample examined, the value of its cell edge is taken as representative of pure magnetite.

The effect of the different ionic substitutions on the cell dimensions of natural magnetites is discussed. An attempt is also made to explain the great variations among the published values of cell dimensions of artificial preparations; one main reason being the presence of defect structures with varying oxygen contents in excess of the formula requirements.

MANY elements may substitute either the divalent or the trivalent atoms in Fe_3O_4, and as a result pure magnetite is the exception and not the rule. A knowledge of the exact value of the cell dimensions of pure natural magnetite is important for any investigation of these different substitutions and their effect on the size of the unit cell.

During a recent study of the system FeO–Fe_2O_3–TiO_2 and the magnetite solid solutions, the author could not find in the literature any reliable data for the unit-cell dimensions of magnetite (Basta, 1953). Holgersson (1927) gave measurements[1] of two natural magnetites from

[1] Throughout this paper, measurements are given in Ångstrom units, converted

Sweden: one from Dalarne with a cell edge of 8·416±0·003 Å., and the other from Nordmarken with a cell edge of 8·429±0·003 Å. However, such measurements are of little value, as they are not accompanied by chemical analyses. Newhouse and Glass (1936), in their study of some physical properties of iron oxides, gave 8·395 Å. for the cell edge of an almost pure magnetite from Lovers' Pit, Mineville, U.S.A.; an averaged value that could not be accepted, especially as it is not known what precautions were adopted in its determination. Very recently, Schmidt and Vermaas (1955) using a 57·3 mm.-diameter camera and unfiltered cobalt radiation gave the values for cell dimensions of five samples of magnetites, from different localities, which range from 8·386 to 8·398 (±0·001) Å. Such relatively large variations of the lattice parameters were attributed to the presence of appreciable amounts of Mg, Al, and in one case Ni; FeO varied between 25 and 28 % indicating an excess of Fe_2O_3. Schmidt and Vermaas plotted the values for cell dimensions against the sum of the molecular proportions of MgO and NiO and concluded that a magnesium-free magnetite should have a cube edge of 8·402 Å. (±0·002). In view of the fact that complete chemical analyses were not given, it is difficult to accept such a conclusion, as other oxides such as TiO_2, MnO, and γ-Fe_2O_3 may enter in the lattice of magnetite and will modify the cell dimensions.[1] A more useful value, however, is 8·392±0·001 Å. given by the same authors for the unit-cell dimensions of the relatively pure Mineville magnetite.

The unit-cell dimensions of magnetite are better known for the artificial compound, but the measurements by different workers range widely from 8·36 Å. to 8·45 Å. (table V).

It is evident that there is a need for reliable and accurate data on the lattice dimensions of such a common mineral as magnetite. A number of chemically analysed magnetite samples were available from an unpublished study of the system FeO–Fe_2O_3–TiO_2. It was therefore decided to utilize some of these samples in the precision determination of the unit-cell dimensions of magnetite; at the same time an attempt was made to explain the considerable variations in the values given by the previous investigators for the artificial preparations. An additional purpose of the work was the possibility of correlating the variations in composition and cell edge of naturally occurring magnetites with the

when necessary from the original values in the references cited (W. L. Bragg, Journ. Sci. Instr., 1947, vol. 24, p. 27). In the absence of a statement of the wave length used, particularly before 1943, the measurements, although usually specified as being in Ångstroms, were presumed to be in kX.

[1] See below, p. 436.

changes in their physical properties, and thus trying to account for some of the contradictory statements as to the appearance of magnetite in polished sections. This part of the work has, however, not progressed sufficiently, and is therefore left for a later publication.

Technique and results of analyses.

Small fragments of selected material were crushed into a fine powder of about 0·1 mm. particle diameter. To avoid iron contamination that

TABLE I. Chemical analyses of magnetites.

	1.	2.	3.	4.	5.	6.		1′.	
FeO	31·43	30·58	31·05	30·76	30·65	31·03	Fe^{2+}	1·024	
MgO	0·18	0·28	0·46	0·19	0·49	—	Mg^{2+}	0·010	3·018
MnO	0·05	0·27	0·03	0·29	0·27	—	Fe^{3+}	1·984	
CaO	0·01	tr.	0·00	tr.	tr.	—	O	4·000	4·000
Fe_2O_3	67·55	66·92	66·42	65·08	68·59	68·97			
Al_2O_3	0·04	tr.	0·37	1·54	tr.	—			
V_2O_3	0·01	n.d.	0·27	n.d.	n.d.	—			
Cr_2O_3	0·02	0·00	0·00	0·00	0·00	—			
TiO_2	0·05	0·28	0·27	0·36	tr.	—			
SiO_2	0·73	1·08	1·22	1·20	0·00	—			
	100·07	99·41	100·09	99·42	100·00	100·00			

1. Magnetite, Bisperg, Säter, Dalecarlia, Sweden. Analyst, H. B. Milner.
2. Magnetite, Barras Nose, Tintagel, Cornwall. Analyst, W. H. Herdsman.
3. Magnetite, Arendal, Norway. Analyst, H. B. Milner.
4. Magnetite, Hall, Ottawa, Canada. Analyst, W. H. Herdsman.
5. Magnetite, recalculated after deduction of 2·02% SiO_2 as quartz, Binnenthal, Switzerland. Analyst, W. H. Herdsman.
6. Theoretical composition of magnetite, Fe_3O_4.

1′. Atomic ratios calculated from analysis 1 on basis of 4 O.

might result if hardened steel mortars were used, the preliminary crushing was carried out between two horizontal disks of non-magnetic Cu-Be alloy under a pressure of 3 to 4 tons per sq. in. The powder was subjected to magnetic and heavy-liquid separations in order to remove impurities (see Basta, 1953, for details). A check for homogeneity was made under the microscope and by X-ray powder photographs.

A specimen of magnetite (Bristol No. 636) from Bisperg, Säter, Dalecarlia, Sweden, was found by chemical and spectrochemical analysis (table I, col. 1) to be exceedingly close to the ideal stoichiometric composition Fe_3O_4. A portion of the analysed sample was studied by X-ray diffraction methods using iron-filtered cobalt radiation in a 114·59 mm.-diameter powder camera of the type described by

W. Parrish and E. Cisney.[1] The change of temperature of the camera during the period of exposure (1½–2 hours) did not exceed 2° C. under operating conditions. The wave-lengths of the X-rays from the cobalt target were taken as $K\alpha_1 = 1{\cdot}78890$, $K\alpha_2 = 1{\cdot}79279$, $K\alpha = 1{\cdot}79020$ Å., and the measurements were made for the specimen at 18° C.

Although the low θ values were indicated by sharp lines, the more important back-reflection lines were diffuse, possibly as a result of lattice distortion or strain of the crystal structure due to the grinding process. Although such a phenomenon is frequently encountered in metals, it has only rarely been reported in minerals, for example by B. Wasserstein[2] in his work on galena; guided by his experience, the powdered magnetite sample was heated to about 400° C. for a few minutes; to safeguard against oxidation, the heating was carried out in evacuated silica glass tubes. X-ray powder photographs of the annealed samples showed a remarkable improvement in definition, which could be attributed to recrystallization. That such recrystallization takes place at the temperature of annealing is supported by the observation made by Gheith (1952), in his work on the differential thermal analysis of iron oxides, that for natural magnetite there is a small exothermic peak at 380–395° C., which he considered to be due to the recrystallization of the finer particles.

Measurements on the films were carried out by means of a Thornton Heath precision instrument equipped with a travelling microscope. Duplicate measurements showed a precision of 0·02 mm. The diffraction lines were measured on either side of the entrance and exit holes of the X-ray beam, and as the Straumanis method of film mounting[3] was used, it was possible to apply accurately the 'shrinkage correction'.

The lattice parameters based on measurements of eight lines from 1·0922 to 0·9386 Å. (see table II) were extrapolated according to the method of Nelson and Riley[4]; the cell edge determined by this extrapolation was 8·3963 Å. (fig. 1).

Another photograph of the same specimen taken with nickel-filtered copper radiation ($Cu\text{-}K\alpha_1 = 1{\cdot}5405$, $Cu\text{-}K\alpha_2 = 1{\cdot}5443$, $Cu\text{-}K\alpha = 1{\cdot}5418$ Å.), although slightly fogged owing to fluorescent radiation, gave the result of 8·3965 Å. for the cell edge, which, despite a small error, shows with what precision results can be duplicated. It was also

[1] Philips Techn. Review, 1948, vol. 10, p. 157 [M.A. **11**–278].
[2] Amer. Min., 1951, vol. 36, p. 102 [M.A. **11**–316].
[3] M. E. Straumanis, Journ. Appl. Physics, 1949, vol. 20, p. 726.
[4] J. B. Nelson and D. P. Riley, Proc. Phys. Soc., London, 1945, vol. 57, p. 16

possible to duplicate the results when different samples from the same locality were similarly examined; a sample of Bisperg magnetite (British Museum, No. 89240) showed very little variation in results from those of the original chemically analysed sample. The complete measurements

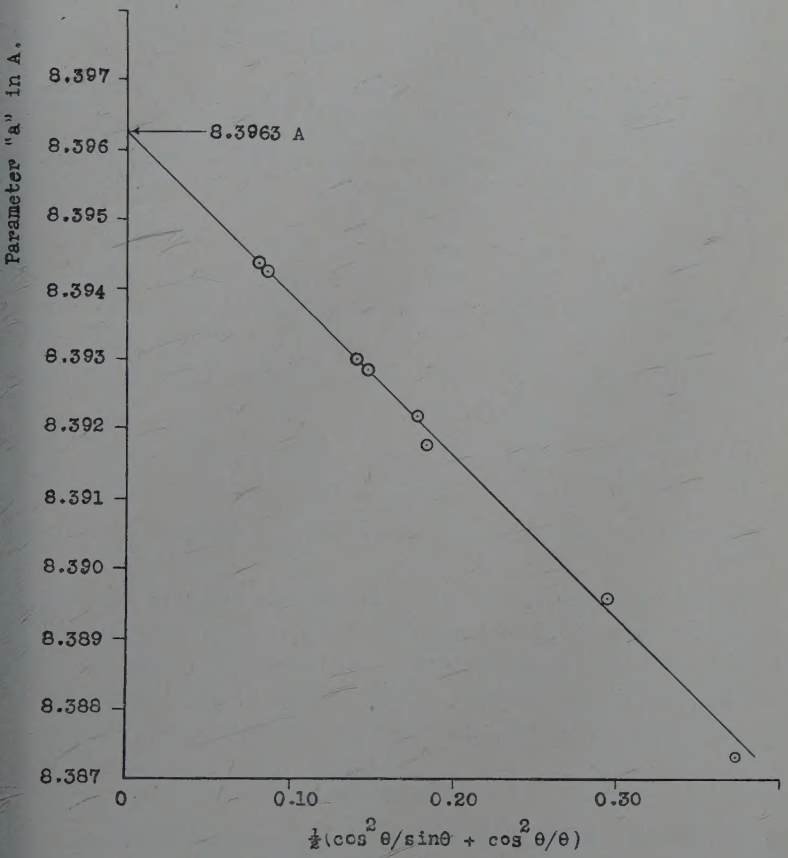

FIG. 1. Extrapolation for the accurate determination of the lattice parameter of Bisperg magnetite at 18° C.

of the X-ray powder pattern of the Bisperg magnetite are given in table II; the spacings recorded show fairly good agreement with the calculated data.

Errors in temperature are considered to be less than one degree, which in terms of the value of cell dimension amounts to an error of less than 0·0001 Å. The positive correction for refraction for magnetite is 0·0001 Å.,

calculated according to the method of Lipson and Wilson[1] (1941), and has been neglected. Taking into account factors of X-ray absorption, thermal expansion, sharpness of the lines, elimination of strain, and the like, the limit of error can be safely taken as 0·0005 Å.

Four other samples of practically pure magnetite from different localities, which have also been chemically analysed (table I, cols. 2

TABLE II. X-ray powder pattern of magnetite, Bisperg, Säter, Sweden; Co-$K\alpha$ radiation. Camera diameter 114·59 mm. Intensities estimated visually. a 8·3963 ± 0·0005 Å. Spacings are compared with those from the A.S.T.M. index card d 1–1120, recommended by the Joint Committee as the best data for magnetite. These data are given by J. D. Hanawalt, H. W. Rinn, and L. K. Frevel, Ind. Eng. Chem., 1938, vol. 10, p. 457.

I.	*d*(obs.)	*hkl.*	*d*(calc.)	$1-\frac{d}{1120}$	*I.*	*d*(obs.)	*hkl.*	*d*(calc.)	$1-\frac{d}{1120}$
mw	4·847	111	4·847	4·85	ms	1·0922α_1	553, 731	1·0930	1·09
s	2·966	220	2·968	2·97	mw	1·0489α_1	800	1·0495	1·05
vvs	2·530	311	2·532	2·53	vvw	0·9890α_1	660, 822	0·9895	—
vvw	2·419	222	2·423	2·42	vvw	0·9890α_2	660, 822	0·9895	—
s	2·096	400	2·098	2·10	mw	0·9692α_1	555, 751	0·9695	0·97
ms	1·712	422	1·714	1·71	w	0·9692α_2	555, 751	0·9695	0·97
vs	1·614	333, 511	1·616	1·61	w	0·9386α_1	840	0·9387	0·94
vs	1·483	440	1·484	1·48	vw	0·9386α_2	840	0·9387	—
vw	1·327	620	1·328	1·33	mw*	0·8794α_1	931	0·8800	0·88
w	1·279	533	1·281	1·28	m*	0·8565α_1	844	0·8589	0·86
vvw	1·264	622	1·266	—	w*	0·8565α_2	844	0·8589	0·85
vw	1·2112	444	1·2120	1·21	mw*	0·8113α_1	951	0·8115	0·81
w	1·1214	642	1·1220	1·12	vw*	0·8113α_2	951	0·8115	0·81

* Measurements of these five lines were obtained from a photograph taken with Cu-$K\alpha$ radiation.

to 5), were examined in the same way and the values of their lattice parameters were found to range from 8·3960 to 8·3970 Å. In view of the fact that the Bisperg magnetite was the purest sample examined, it is proposed to take its value, 8·3963±0·0005 Å., as representative of pure magnetite until such time as a purer specimen is measured.

Discussion.

Analyses of natural magnetites show that they frequently contain other cations, which may substitute either the divalent or the trivalent iron and may modify the cell dimensions. Table III shows that among the divalent elements that may enter the crystal structure of magnetite, only Mn^{2+} has an ionic radius greater than that of Fe^{2+}, while all the trivalent elements have an ionic radius less than that of Fe^{3+}. From the table it is clear that the cell dimensions of magnetite are increased only when replacement by Mn^{2+} or Ti^{4+} takes place; the cell-edge values of the spinels $MnFe_2O_4$ and Fe_2TiO_4 thus formed are 8·51

[1] H. Lipson and A. J. C. Wilson, Journ. Sci. Instr., 1941, vol. 18, p. 144.

and 8·50 Å. respectively (Bénard and Chaudron, 1937; Pouillard, 1949). However, manganese is rarely present in appreciable amount and natural magnetite ores usually contain less than 3% MnO corresponding to 10% $MnFe_2O_4$. Ulvöspinel, Fe_2TiO_4, on the other hand, has been shown

TABLE III. Ionic radii of the elements that may enter the crystal structure of magnetite, and the cell dimensions (in Å) of the spinels thus formed (various authorities).

Metal.	Ionic radius.	Al^{3+} 0·57.	Cr^{3+} 0·64.	Fe^{3+} 0·67.	Ti^{4+} 0·64.
Ni^{2+}	0·78	*a* 8·05	*a* 8·30	*a* 8·36	—
Mg^{2+}	0·78	8·07	8·31	8·37	—
Co^{2+}	0·82	8·08	8·32	8·38	—
Zn^{2+}	0·83	8·07	8·30	8·40	—
Fe^{2+}	0·83	8·12	8·34	8·40*	*a* 8·50
Mn^{2+}	0·91	8·26	8·49	8·51	—

* The value of cell edge for magnetite as determined in this paper, simplified to three significant figures.

TABLE IV. Chemical analyses of some substituted magnetites and their cell dimensions.

	1.	2.	3.		1′.	2′.	3′.
FeO	42·33	21·83	12·75	$FeFe_2O_4$	33·18	39·9	35·1
MgO	2·07	7·18	0·91	$MgFe_2O_4$	4·67	28·8	4·6
MnO	0·72	1·82	0·18	$MnFe_2O_4$	2·31	6·0	—
CaO	—	0·94	0·76	$CaFe_2O_4$	—	3·7	2·4
Fe_2O_3	26·88	57·11	80·63	γ-Fe_2O_3	—	—	53·0
Al_2O_3	0·40	3·62	0·30	$MgAl_2O_4$	—	5·1	—
V_2O_3	—	0·10	0·12				
Cr_2O_3	—	0·01	0·01	Fe_2TiO_4	32·48	10·3	—
TiO_2	24·86	6·98	2·54	γ-$FeTiO_3$	27·36	6·2	4·9
SiO_2	2·64	0·38	0·84		100·00	100·0	100·0
	99·90	99·97	99·04				

1. Titanomagnetite separated from basalt, Giant's Causeway, Ireland. Anal. W. H. Herdsman. $a = 8{\cdot}4697 \pm 0{\cdot}0005$ Å.

2. Titanomagnetite from Magnet Cove, Arkansas, U.S.A. Anal. H. B. Milner. $a = 8{\cdot}3960 \pm 0{\cdot}001$ Å.

3. Magnetite-maghemite separated from basalt, Co. Antrim, Ireland. Anal. H. B. Milner. $a = 8{\cdot}369 \pm 0{\cdot}001$ Å.

1′, 2′, 3′ are the percentages of the end-members calculated from the analyses 1, 2, and 3.

to be more common than had previously been supposed (Basta, 1953; Ramdohr, 1953; Vincent and Phillips, 1954). The present author, working on carefully separated homogeneous titanomagnetites from volcanic rocks, has found up to 32·5% Fe_2TiO_4 (table IV, col. 1), a substitution that results in a continuous increase in the cell dimensions.

Replacements of Fe^{2+} or Fe^{3+} in magnetite by other divalent or

trivalent ions, e.g. Mg^{2+}, Co^{2+}, Ni^{2+}, Al^{3+}, and Cr^{3+}, also occur, but the effect in these cases is a decrease in the cell dimensions of magnetite. Exceptionally up to 8 % MgO (table IV, col. 2) and up to 7 % Al_2O_3 have been recorded in the analyses of magnetites, but such values are uncommon. Contents of ZnO, NiO, CoO, and Cr_2O_3 are usually too low to influence the cell-edge value of natural magnetite significantly. Zn reported by Vincent and Phillips (1954) in their analyses of magnetites from the Skaergaard intrusion, East Greenland, did not exceed 0·2 %; Schmidt and Vermaas (1955) determined 1·76 % NiO in one of their specimens of magnetite from Witbank, S. Africa; Cr_2O_3 is usually less than 0·5 %. V_2O_3 rarely exceeds 2 %, corresponding to a replacement of less than 3 % of the Fe^{3+} ions by V^{3+}, but its effect on the cell dimensions is not known. Another possibility leading to a decrease in the size of the unit cell of natural magnetites is partial oxidation to maghemite ($a = 8{\cdot}32$ Å.). In an unpublished study (Basta, 1953), the author was able to prove, by chemical and X-ray analyses, the existence in nature of minerals intermediate in composition between Fe_3O_4 and γ-Fe_2O_3; one of the analyses is given in table IV, col. 3.

Since several substitutions are possible, some increasing and some decreasing the cell dimensions, it is impossible to deduce the chemical composition of natural magnetite from the cell dimensions alone; even if the unit cell has the size of that of pure Fe_3O_4 there may be substantial substitutions, as in the Magnet Cove titanomagnetite (table IV, col. 2).

Variations in the chemical composition and cell edge of naturally occurring magnetite may account for the considerable differences in its physical properties reported in the literature; thus figures for the specific gravity vary between 4·96 and 5·3. From the present X-ray data on the Bisperg magnetite, its specific gravity was calculated as 5·192.

Literature data for the cell dimensions of artificial magnetite show marked variations (table V).

The values given by earlier workers up to 1940 may not be quite as precise as indicated, for at the time when these measurements were made the nature of the systematic errors was not fully known, the wavelength values assumed for the various radiations differ appreciably from the present values, and the cited lattice parameters were usually averages of the values calculated from all the lines of both low and high angle θ. Thus the measurement of Clarke, Ally, and Badger (1931), which is that given in the 7th edition of Dana's System of Mineralogy[1]

[1] C. Palache, H. Berman, and C. Frondel, Dana's System of Mineralogy, 7th edn., New York, 1944, vol. 1, p. 698.

and in Wyckoff's Crystal Structures[1], requires revision. In their original paper, the value of 8·374±0·003 Å. was obtained from measurements with a scale reading directly in lattice spacings. The two values listed in table V were obtained by conversion, firstly to Ångstrom units from the wave-length 0·712 [kX] quoted for the Mo radiation used, secondly from the wave-length 0·70783 kX then known for Mo-*K*, by which the scale may have been calibrated. The exceptionally high value obtained by Van der Marel (1951) is most probably owing, as the author himself indicated, to the presence of impurities, possibly Na, in his

TABLE V. Cell edge of Fe_3O_4 (Å.).

Holgersson (1927)	8·434
Clarke, Ally, and Badger (1931)	8·361±0·003 or 8·389±0·003
Hägg (1935)	8·397
Gaglioti and D'Agostino (1936)	8·427
Bénard (1939)	8·390±0·002
Frank-Kamenecky (1939)	8·437
Pouillard (1949)	8·413
Van der Marel (1951)	8·441±0·004
Tombs and Rooksby (1951)	8·3940±0·0005
Abrahams and Calhoun (1953)	8·3940±0·0005
Basta, on Bisperg magnetite, this paper	8·3963±0·0005

samples, which were prepared by precipitation. Michel (1937, p. 37) has found that up to 7 % of the Fe^{2+} ions of synthetic magnetites may be replaced by Na^{+} and Fe^{3+}, a replacement that causes the cell dimensions to rise from 8·41 to 8·43 Å.

An important possibility that may account for the distinct range of 8·36 to 8·44 Å. in values of the cell edge obtained by different workers on artificial preparations is the presence of oxygen in excess of the stoichiometric formula requirements, as has already been mentioned in the case of natural magnetite. Hägg (1935) found that magnetite, when oxidized at up to 300° C., may vary continuously in composition from Fe_3O_4 to $Fe_{8/3}O_4$, i.e. to γ-Fe_2O_3, the cell edge decreasing uniformly from 8·40 to 8·32 Å. Furthermore, from the work of Greig and his co-workers (1935), magnetite is capable of containing about 30 % Fe_2O_3 at 1452° C.; the product gives an X-ray powder pattern of the spinel type but with a value of the cell edge slightly lower than that of pure Fe_3O_4. The artificial preparations of Fe_3O_4 on which the cell dimensions quoted in table V were measured were made either from slags, the so-called hammer-scale (Holgersson, 1927); or by heating at up to 1300° C. preparations containing Fe^{2+} and Fe^{3+} in the atomic

[1] R. W. G. Wyckoff, Crystal Structures, 1952, vol. 2, New York.

ratio 1:2 (Clark, Ally, and Badger, 1931); or by reducing hematite at high temperatures, up to 1400° C., with hydrogen. In none of these preparations was a check made on the $Fe^{2+}:Fe^{3+}$ ratio after heating. An increase of oxygen, i.e. a decrease in iron beyond the formula requirement, may well have occurred, and may be the reason for the low values of the cell edge as observed in some of the preparations. Starke (1939) sought to explain the relation of the structure of synthetic magnetite to its stability by assuming that the unit cell of precipitated magnetite contains: 16 Fe^{3+}, $5\frac{1}{3}$ Fe^{2+}, $26\frac{2}{3}O^{2-}$, $5\frac{1}{3}OH^{-}$, and not $16Fe^{3+}$, $8Fe^{2+}$, $32O^{2-}$, as in the case of the high-temperature magnetite.

Recalculation of the chemical analysis of the Bisperg magnetite (table I, col. 1′) gave the formula $Fe^{2+}_{1\cdot024}Mg^{2+}_{0\cdot010}Fe^{3+}_{1\cdot984}O_{4\cdot000}$; the ratio of total cations to oxygen was 3·018:4·000, which shows that such a magnetite is free from vacant cation positions. Similar calculations on the four other new analyses in table I led to the same conclusion.

Another factor that may influence the cell dimensions of magnetite is the possibility of cation rearrangement. The equality of the scattering power of Fe^{2+} and Fe^{3+} makes it impossible to decide from the X-ray data whether magnetite is a normal spinel, $X^{2+}Y^{3+}_2O_4$, with divalent atoms in the eightfold and trivalent in the sixteenfold positions, or an inversed spinel, $Y^{3+}(X^{2+}Y^{3+})O_4$, with trivalent atoms in the eightfold positions and the sixteenfold positions divided between di- and trivalent atoms.

Verwey and De Boer (1936) assigned magnetite to the inversed group on account of its high electrical conductivity, and Verwey and Heilmann (1947) arrived at the same conclusion from a consideration of the cell dimensions of a large number of spinels.[1]

It is possible that at high temperatures there is a more random distribution of the cations, or that a partial change to the normal spinel structure takes place. If this is so, small variations in the cell dimensions of pure Fe_3O_4 may occur after heating, varying with the temperature attained and the rate of cooling; further work is needed to test this suggestion. A change in the cation arrangement at high temperatures has been found for some other members of the spinel group ($AlFe_2O_4$, Verwey, Hayman, and Raneijn, 1947; $MnFe_2O_4$, McAndrew, 1952).

[1] Verwey and Heilmann found that normal ferrites generally have a unit cell about 0·12 Å., larger than that of the corresponding chromites, while for inversed ferrites the increase is only about 0·05 Å.; for the pair $FeCr_2O_4$–Fe_3O_4 the increase is 0·06 Å (see table III).

Conclusions.

The great variation among the reported cell dimensions of artificially prepared magnetites is mainly owing to the formation of defect structures with varying oxygen contents in excess of the formula requirements. Another possible cause of variation is change in the cation arrangement in the spinel structure of magnetite at high temperatures, depending on the method of preparation.

The Bisperg magnetite, which has the formula

$$Fe^{2+}_{1\cdot024}Mg^{2+}_{0\cdot010}Fe^{3+}_{1\cdot984}O_{4\cdot000},$$

is substantially free from defect structures, and from accurate X-ray determinations carried out on annealed specimens free of crystal distortion the following result was obtained for its cell edge and is suggested to be the best known value for pure natural magnetite: a at 18° C. = 8·3963±0·0005 Å.

An appreciable increase in the cell dimensions of natural magnetite above this value probably indicates the presence of Fe_2TiO_4 or $MnFe_2O_4$ in solid solution, while an appreciable lowering of the above value may indicate partial oxidation to γ-Fe_2O_3. Other substitutions of Fe^{2+} or Fe^{3+} in the magnetite lattice by Mg^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cr^{3+}, Al^{3+}, or V^{3+} occur but they are of minor importance, either because the cell dimensions of the resultant spinel are not much different from those of pure magnetite or because the extent of substitution is very limited in natural ores. In all cases it is impossible to predict the exact composition from cell dimensions alone.

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Titanomagnetites from a differentiated teschenite sill.

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Summary. Mineragraphic, chemical, and X-ray data are presented on the titanomagnetites[1] from a differentiated teschenite sill. The minerals are generally homogeneous. The earliest titanomagnetites are Fe_3O_4.Fe_2TiO_4.$FeTiO_3$ solid solutions; the titanomagnetite crystallization trend is one of enrichment in Fe_3O_4 and $FeTiO_3$ at the expense of Fe_2TiO_4. The relations of the titanomagnetites to the parent rocks and associated minerals, and their role in basaltic magma iron enrichment are also discussed.

WHILE mineragraphic data are available on the opaque minerals of common igneous rocks (Newhouse, 1936) and certain volcanic suites (e.g. Odman, 1932; Cornwall, 1951), the recent detailed mineragraphic and chemical investigation of Vincent and Phillips (1954) on the iron–titanium oxide minerals of the tholeiitic Skaergaard intrusion constitutes one of the few studies on the opaque oxides from a genetically related intrusive series. The present study embraces certain aspects of the iron–titanium oxide minerals from a differentiated teschenite sill, Tertiary in age and approximately 500 feet thick, situated three miles south-west of Gunnedah, New South Wales.

Polished sections were prepared of specimens B1, B2, B3, B4, B7, B9, and H8, teschenites approximately 20, 20, 120, 270, 420, 500, and 500 feet above the lower intrusion contacts. Chemical analyses are available of the parent rocks. Modal and trace element data on the titanomagnetites will be discussed in more detail in a separate paper.

Microscopic study of the opaque minerals.

The monotony of the mineralogy and a general homogeneity within individual grains constitute the most important features of reflected-light studies. Titanomagnetite[1] predominates, while ilmenite is rare.

[1] The term 'titanomagnetite' is used to denote a single-phase solution of TiO_2 compounds in magnetite (Ramdohr, 1926, p. 345; Buddington, Fahey, and Vlisidis, 1955, p. 498). Although both X-ray and chemical data on the titanomagnetites

All the sections carry droplets of sulphide. Hematite and rutile were not identified.

Except for rare exsolution lamellae enriched in $FeTiO_3$ the titanomagnetite is homogeneous in all the polished sections. Although analyses of this mineral from specimens B1 and B4 (table I, analyses 1 and 2) indicate considerable amounts of Fe_2TiO_4, the titanomagnetite,

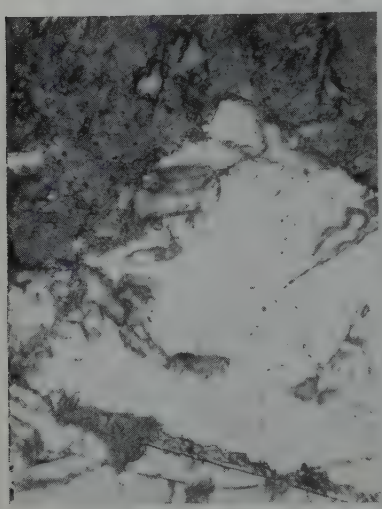

Fig. 1 (*left*). Portion of titanomagnetite crystal from specimen B1 (analysed), indicating the absence of any exsolution structures. The polished section has been etched with HF. (Reflected light ×700.)

Fig. 2 (*right*). Skeletal titanomagnetite from teschenite E8, 410 feet above the lower contact. The titanomagnetite is moulded against olivine (O) and plagioclase (P). (Ordinary transmitted light ×13.)

even after etching with HF and under high magnification, still retains its homogeneity (fig. 1) with no indication of the characteristic 'cloth' texture' of exsolved ulvöspinel. Despite their relatively high TiO_2 content, the titanomagnetites are also homogeneous with respect to exsolved ilmenite. In rare cases *faintly* anisotropic lamellae representing initial stages in the unmixing of $FeTiO_3$ are observed. Occasional titanomagnetite phenocrysts also reveal a similar degree of anisotropism resulting from Fe_3O_4–$FeTiO_3$ solid solutions (Edwards, 1954, p. 76).

indicates the presence in solid solution of the iron-titanium spinel Fe_2TiO_4 (ulvöspinel), this mineral has not been detected as a separate phase, and hence is referred to in general by its chemical formula only (following Vincent and Phillips, 1954, p. 3).

The titanomagnetites are often altered internally to deuteric silicate, sometimes recognizable either as sphene or leucoxene. The leucoxene sometimes shows faint relic structures suggesting its derivation from previous exsolved lamellae. It would be anticipated that such exsolution products, enriched in $FeTiO_3$, would be more susceptible to leucoxenization. This alteration to silicate is not considered responsible for the intricate skeletal outlines (cf. Odman, 1932, p. 288) in the titanomagnetite from the upper levels of the sill (fig. 2). In reflected light the adjacent silicate generally presents knife-edge contacts against the titanomagnetites and in the areas between the branching titanomagnetite 'arms'. The degree of idiomorphism of the magnetite tends to vary with its position in the crystallization sequence, the skeletal ores indicating a later crystallization. The titanomagnetites frequently curve around plagioclase and adjoining ferro-magnesian silicates. Newhouse (1936, p. 25) and Osborne (1928, p. 749) have summarized opinions dealing with the late crystallization of the opaque oxides in many basic rocks.

Homogeneous ilmenite was detected as scattered rare grains in B2 and H8. The degree of homogeneity of the titanomagnetite, and the absence of this mineral in the vicinity of the ilmenite grains, suggests that the ilmenite is a primary precipitation mineral and not an exsolution product of Fe_3O_4–Fe_2TiO_4–$FeTiO_3$ solid solutions (cf. Vincent and Phillips, 1954, p. 6).

The data on the opaque oxides from hypabyssal alkaline basic rocks appear to be meagre. In volcanic representatives Newhouse (1936, tables 11–12) recorded only magnetite in seventeen nepheline- and leucite-basalts. Ilmenite was absent. On the other hand, in sixty-five gabbros, diabases, and allied rocks studied by Newhouse, ilmenite and ilmenite–magnetite intergrowths were the most important opaque oxides. Homogeneous magnetite was found to be comparatively rare.

The minor amounts of sulphides appear to be more abundant in the teschenites from the upper levels of the sill. Chalcopyrite predominates over pyrite. As in the Duluth gabbro (Schwartz, 1930, p. 250), the sulphides generally occur as granules disseminated interstitially to the silicates. Chalcopyrite in analcime veinlets was noted in H8.

Chemical and X-ray data on the titanomagnetites.

The three analysed titanomagnetites (table I, analyses 1–3) have been recalculated into possible spinel molecules, ilmenite, and silicates, following the method applied by Mogensen (1946) and by Vincent and

Phillips (1954). The titanomagnetite chemistry reveals an excess o FeO when an attempt is made to interpret the analyses solely on a basi

TABLE I. Chemical analyses of titanomagnetites, with a recalculation into end members following Mogensen (1946) and Vincent and Phillips (1954).

	1.	2.	3.	4.	5.	6.	7.	8.	9.
SiO_2	0·33	0·54	2·85	0·24	0·23	—	1·81	—	—
TiO_2	26·76	27·29	29·66	19·28	23·74	18·41	15·30	18·02	14·03
Al_2O_3	2·31	3·55	2·45	0·78	0·91	2·35	6·16	—	—
Fe_2O_3	21·10	23·18	30·21	32·27	31·26	27·93	32·39	36·03	40·62
FeO	45·22	41·86	29·32	43·07	41·69	45·82	36·67	43·89	44·12
MnO	0·61	0·69	1·17	0·33	0·45	0·42	0·43	0·93	0·74
MgO	1·93	2·33	0·79	1·98	1·21	2·48	4·37	—	—
CaO	0·59	0·27	2·63	0·42	tr.	0·73	0·16	—	—
V_2O_3	0·37*	0·44*	0·30*	1·74	0·40	0·92	0·86	1·13	0·49
Cr_2O_3	0·38*	0·10*	nil*	0·13	nil	0·94	n.d.	—	—
S	n.d.	n.d.	0·09	—	—	—	—	—	—
&c.	—	—	—	0·09	0·11	—	1·36	—	0·004
Total	99·60	100·25	99·47	100·33	100·00	100·00	99·51	100·00	100·00

* These constituents were determined spectrographically.

Recalculated compositions (wt. %)

$CaO.SiO_2$	0·58	0·58	—	0·46	—	—	0·35	—	—
$MgO.SiO_2$	—	0·40	0·10	—	0·38	—	2·70	—	—
$FeO.SiO_2$	—	—	—	—	—	—	—	—	—
$MgO.Al_2O_3$	3·27	4·83	2·70	1·08	1·27	3·3	8·67	—	—
$FeO.Al_2O_3$	—	—	0·87	—	—	—	—	—	—
$CaO.Fe_2O_3$	1·30	—	—	0·75	—	2·8	—	—	—
$MgO.Fe_2O_3$	5·00	4·00	—	8·30	3·46	7·6	4·20	—	—
$MnO.Fe_2O_3$	2·08	2·31	3·70	1·06	1·45	1·4	1·39	3·00	2·31
$FeO.V_2O_3$	0·44	0·67	0·44	2·58	0·60	1·4	1·33	1·78	0·67
$FeO.Cr_2O_3$	0·45	0·22	—	0·18	—	1·4	—	—	—
$FeO.Fe_2O_3$	21·34	26·68	40·14	35·33	39·87	27·6	40·60	49·18	56·61
$FeO.TiO_2$	20·67	33·44	34·51	7·14	28·48	—	8·21	9·12	—
$2FeO.TiO_2$	44·35	27·10	—	43·39	24·40	51·8	30·69	36·96	39·20
FeO.	—	—	—	—	—	2·7	—	—	1·15
TiO_2	—	—	7·68	—	—	—	—	—	—
$CaO.TiO_2.SiO_2$	—	—	9·21	—	—	—	—	—	—
&c.	—	—	—	—	—	—	1·36	—	0·00
Total	99·48	100·23	99·35	100·27	99·91	100·0	99·50	100·04	99·94

Analyses 1–3, titanomagnetites from the Black Jack sill. Anal. J. F. G. W.

1. Titanomagnetite from teschenite B1, 20 feet above lower contact.
2. Titanomagnetite from teschenite B4, 270 feet above lower contact.
3. Titanomagnetite from teschenite H8, approx. 500 feet above lower contact.
4. Magnetite from melanocratic band in hypersthene-olivine-gabbro (2308), Skaergaa intrusion, East Greenland. Anal. E. A. Vincent (Vincent and Phillips, 1954, table 2).
5. Magnetite from melanocratic band in hortonolite-ferrogabbro (2569), Skaergaard intr sion, East Greenland. Anal. E. A. Vincent (Vincent and Phillips, op. cit.).
6. Magnetite from dolerite, Södra Ulvön, Sweden (Mogensen, 1946, p. 586). Compositi of magnetite calculated from analysis of a high grade concentrate containing 1·61 % Si (2·5 % other minerals).
7. Magnetite from magnetite-olivinite dyke, Taberg, Sweden. Anal. A. Aaremäe (Hjelmqvi 1950, p. 28).
8 and 9. Magnetites from Japanese augite-olivine-basalts (recalculated to 100 %). An T. Katura (Taneda, 1950, table 2).

of Fe_3O_4–$FeTiO_3$ solid solutions. In other titanomagnetites simila difficulties have been largely resolved by the microscopic and X-ra recognition of exsolved ulvöspinel (table I, analyses 5 and 6). Th

recalculated analyses of titanomagnetites B1 and B4 suggest approximately 44 and 27 % Fe_2TiO_4 in solid solution. In both cases the X-ray powder patterns show only one set of magnetite-spinel lines, with no indication of shadowing of the lines by another spinel of slightly different cell dimensions. Ilmenite lines are absent. The cell dimensions of both these magnetites are a 8·48 Å. (±0·01 Å.). These values are higher than those usually given for naturally occurring and artificial magnetites, namely a 8·36 to 8·42 Å. (Mason, 1943, p. 105). Tombs and Rooksby (1951, p. 474) and Abrahams and Calhoun (1953, p. 105) have determined the cell edge of artificial magnetite as a 8·394 Å. It would be anticipated that titanomagnetite B4, containing less recalculated Fe_2TiO_4 than B1, would have slightly smaller cell dimensions. However, conclusions of this type are not justified until we know more of the effects of constituents other than Fe^{2+}, Fe^{3+}, and Ti on the cell dimensions of the complex solid solutions.

The recalculated analysis of titanomagnetite H8 indicates the absence of Fe_2TiO_4; only magnetite lines are present on the powder photograph, and a = 8·42 Å. H8 is veined with sphene and is also slightly leucoxenized. The recalculated analysis indicates a predominantly Fe_3O_4–$FeTiO_3$ solid solution. In this case the CaO has been allotted for the formation of sphene.

All the Black Jack titanomagnetites are characterized by high TiO_2, and, in B1 and B4, high FeO contents. They show even greater amounts of TiO_2 than some similar titanomagnetites in which exsolution of other phases has occurred (e.g. table I, analyses 5 and 6). The 'ilmenite-magnetite' from Susimäki, Finland (Palmunen, 1925, table 8), listed by Buddington *et al.* (1955, table 6) as a titaniferous magnetite, has FeO 42·81, Fe_2O_3 28·39, and TiO_2 26·12 %; the recalculated Fe_2TiO_4 content is approximately 24 %. The Black Jack minerals are also similar chemically to homogeneous titanomagnetites from volcanic rocks (table I, analyses 8 and 9).[1] Akimoto (1951, table I) lists a magnetite from an olivine-basalt, Kwanto district, Japan, with FeO 43·89, Fe_2O_3 36·03, and TiO_2 18·02 %.

The alumina in all three analyses (see also table I, analyses 6 and 7) is probably present in spinel molecules, principally $MgAl_2O_4$, in solid solution. Approximately 2 % MgO is present in B1 and B4, decreasing

[1] Dr. E. Z. Basta (unpubl. thesis, University of Bristol; this vol., p. 431) has described homogeneous titanomagnetites from volcanic rocks whose chemistry, cell dimensions, and recalculated compositions are very similar to titanomagnetites B1 and B4.

in amount in H8 as less magnesia became available from the magma. Under conditions of slow cooling, the spinel may exsolve from the magnetite, along with ulvöspinel (Hjelmqvist, 1950, figs. 29 and 30; Girault, 1953, figs. 2 to 4; Vincent and Phillips, 1954, p. 4). In both the Black Jack and Skaergaard titanomagnetites there is an increasing proportion of MnO to FeO with magmatic evolution (cf. Goldschmidt, 1954, p. 631).

General Discussion.

The concept of Fe_3O_4–Fe_2TiO_4–$FeTiO_3$ *solid solutions.* Pouillard and Michel (1949) and Pouillard (1950) have prepared continuous solid solutions between Fe_3O_4 and Fe_2TiO_4, whose members show an increase in cell dimensions compared with pure Fe_3O_4. In a synthetic titanomagnetite of this type prepared by Pouillard (op. cit., p. 199), and containing 42 molecular % Fe_2TiO_4, the cell dimensions were a 8·46 Å., compare titanomagnetite B1. Chevallier and Girard (1950) have synthesized titanomagnetites possessing the magnetite structure with a 8·300 to 8·412 Å.[1] whose compositions may be expressed by the general formula $y Fe_3O_4.(1–y)FeTiO_3$. These authors suggest that natural titanomagnetite is probably composed of the Fe_3O_4–Fe_2TiO_4 series with some of the Fe_3O_4–$FeTiO_3$ series also in solid solution. This appears to be the case in titanomagnetites B1 and B4. The homogeneity of these minerals, comparable to that of volcanic titanomagnetites, resulted from the relatively rapid cooling attendant on a small volume of magma crystallizing under near-surface conditions. The homogeneity of the titanomagnetites in the upper teschenites was aided also by their relatively late position in the crystallization sequence. In the Black Jack sill the titanomagnetites are not the only solid solution series prone to unmixing that has failed to unmix. Anorthoclase (Or_{26}) from a teschenite 450 feet above the lower contacts is homogeneous as revealed by the X-ray powder photograph; the spectrometer pattern reveals only slight submicroscopic unmixing.

It should be noted that in other naturally occurring titanomagnetites with excess FeO, the exsolved material with a 8·47 to 8·48 Å. has been referred to as ulvöspinel (Mogensen, 1946, p. 586; Girault, 1953, p. 307 Vincent and Phillips, 1954, p. 11). These cell dimensions are less than those of synthetic Fe_2TiO_4, namely a 8·50 Å. (Barth and Posnjak, 1932 p. 341) or a 8·534 Å. (Pouillard, 1950, p. 199). It may well be that in the above examples complete unmixing of ulvöspinel had not ye

[1] The value 8·300 Å. seems improbably low; perhaps it is a misprint.

occurred, and that the unmixing of Fe_3O_4–Fe_2TiO_4 solid solutions is of a progressive type whereby magnetite (*a* 8·37 to 8·39 Å.) may separate as one end member, the other phase being predominantly an Fe_3O_4–Fe_2TiO_4 solid solution that might yield ulvöspinel on extremely slow cooling. In certain cases it seems likely that the composition of the initial homogeneous solid lies slightly to the left of the eutectoid *E* in the phase diagram for Fe_3O_4–Fe_2TiO_4 given by Phillips (in Vincent and Phillips, 1954, fig. 2). The problem warrants further attention;

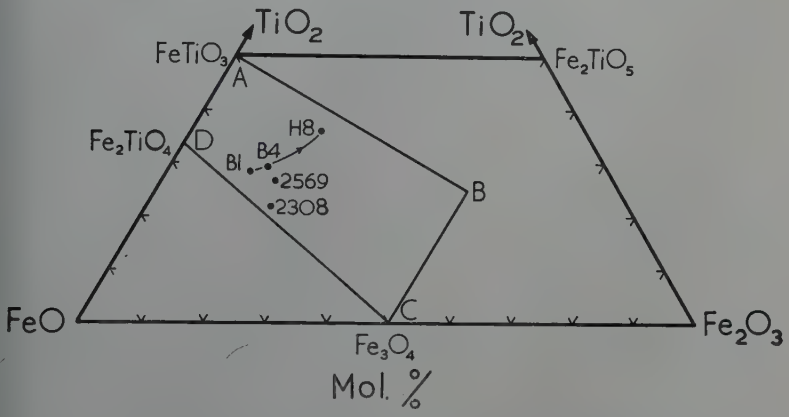

FIG. 3. The Black Jack titanomagnetites plotted on the system $FeO.Fe_2O_3.TiO_2$. The titanomagnetite crystallization trend is B1→H8. 2308, 2569 are magnetites from the Skaergaard intrusion, E. Greenland (Vincent and Phillips, 1954, table 2.)

a full assessment of the unmixing process is probably complicated by oxidation-reduction reactions during exsolution, and the complex nature of the original solid solutions.

The initial decrease and final disappearance of Fe_2TiO_4 in the Black Jack titanomagnetites substantiate the contention of Foslie (1928) that ulvöspinel does not form in the presence of excess Fe_2O_3. With progressive teschenite differentiation, ferric iron progressively increased in those liquids from which the upper titanomagnetites crystallized.

Crystallization trend of the titanomagnetites and relations to the parent rocks and associated minerals. In fig. 3 the titanomagnetites have been plotted on the system $FeO.Fe_2O_3.TiO_2$. All the Black Jack minerals fall in the field *ABCD*, comprising ores composed of two dominant phases, a titanomagnetite and an ilmenite. The titanomagnetite crystallization trend is towards the area of low melting in the as yet

incompletely determined $FeO.Fe_2O_3.TiO_2$ thermal system (Ernst, 1943, fig. 1), and involves enrichment in Fe_3O_4 and $FeTiO_3$ at the expense of Fe_2TiO_4; it is consistent with similar temperature trends indicated by the compositions of the associated olivines, clinopyroxenes, and plagioclase felspars. The variation in the principal oxides with falling temperature is a decrease in FeO whilst Fe_2O_3 and TiO_2 both increase (cf. Buddington *et al.*, 1955, pp. 516–517). Considering variation with respect to FeO in the principal ferriferous minerals of the teschenites, the titanomagnetite undergoes variation slightly less (45 to 29 % FeO) than the olivines (20 to 48 %). The clinopyroxene (6·6 to 10 % FeO) is the least susceptible to compositional change.

G. C. Kennedy (1948) has stressed the importance of the ferric–ferrous iron ratio in petrology, the concentration or pressure of water vapour playing an important role in the state of oxidation of the iron in the rock melt. With increasing height in the Black Jack sill, concomitant with progressive differentiation, the increasing activity of the late-stage solutions, in some instances iron-rich, becomes more pronounced, effecting a wide variety of mineralogical alteration, solution, and redeposition. The analcimization of the plagioclase and the deposition of analcime and a highly ferriferous carbonate in small vughs, the precipitation of an iron-charged mesostasis, the alteration of the olivine to bowlingite, and also to iddingsite (when the residual solutions had become enriched in ferric iron, compare Edwards, 1938, pp. 280–281), are all changes essentially deuteric in the original sense of Sederholm. The ferric–ferrous iron ratio of the teschenites increases during differentiation (table II), a relationship emphasized by Goldschmidt (1954, pp. 34 et seq.). Although the Fe_2O_3/FeO ratios for both the parent rocks and the associated titanomagnetites are approximately the same in the early stages of consolidation, this ratio increases much more rapidly for the ores than for the rocks. The Fe_2O_3 of the residual liquids was constantly built up during differentiation so that the titanomagnetites in the upper teschenites, dominantly late crystallization products, are enriched in this constituent.

Discussing the differentiation of titaniferous magmas, Evrard (1949, p. 213) points out that in general the ratio of titania to the total iron oxides increases with increased differentiation. The degree of differentiation of the teschenites is best expressed by the ratio $(FeO+Fe_2O_3)/(FeO+Fe_2O_3+MgO)$, which in table II is compared with the molecular ratios $TiO_2/(TiO_2+FeO+Fe_2O_3)$ (after Evrard, op. cit.). This latter ratio does reveal a general increase with differentiation. In the lavas

of the Keeweenawan Series in Michigan the ratio $TiO_2/(TiO_2+FeO+Fe_2O_3)$ also increases with differentiation (Cornwall, 1951*a*, p. 64).

The relations of the opaque iron-titanium oxide minerals to iron enrichment in basic magma. The debatable question of whether the residual liquids of basaltic magmas undergo enrichment in iron has attracted the attention of petrologists for many years (Fenner, 1929, 1931; Bowen, 1928; Edwards, 1942; Walker and Poldervaart, 1949). The

TABLE II. Differentiation ratios for the Black Jack teschenites and their associated titanomagnetites.

$$\left(t=\frac{TiO_2}{TiO_2+FeO+Fe_2O_3}\times 100,\ \text{mol. \%};\quad f=\frac{FeO+Fe_2O_3}{FeO+Fe_2O_3+MgO}\times 100,\ \text{wt. \%}\right)$$

Specimen number.	Height in feet above lower contact.	FeO.	Fe_2O_3.	TiO_2	*t*.	*f*.	$\frac{Fe_2O_3}{FeO}$
Rocks							
B1	20	9·15	4·15	2·49	16·9	58·2	0·45
B2	20	9·51	2·93	2·58	18·0	60·6	0·31
B3	120	8·36	2·59	2·71	20·5	69·7	0·31
B4	270	9·28	3·12	2·62	18·2	62·4	0·34
B7	420	7·93	2·71	2·79	21·6	69·8	0·34
B9	500	9·43	3·83	4·07	24·8	72·6	0·41
H1	approx. 500	9·48	3·20	3·60	22·9	78·2	0·34
H8	approx. 500	9·57	4·15	3·53	21·5	82·2	0·43
H4	approx. 500	5·49	3·26	0·59	76·2	95·4	0·59
Titanomagnetites							
B1	—	45·22	21·10	26·76	30·5	—	0·47
B4	—	41·86	23·18	27·29	32·0	—	0·55
B8	—	29·32	30·21	29·66	38·3	—	1·03

B1–H8 teschenites. H4 is an analysis of a vein of microcrystalline mesostasis (analcime-syenite in composition) from the teschenite H4.

Black Jack teschenites, representatives of alkali olivine-basalt magma, reveal only slight absolute iron enrichment in the later stages of evolution, not on any scale comparable with the tholeiitic Skaergaard rocks. It has been argued that this latter type of differentiation, namely absolute enrichment in iron in basic magma for the greater part of its crystallization history, is abnormal in type. That this does not appear to be the case is illustrated by absolute iron enrichment trends in the New Amalfi, Breven, Hällefors, Beaver Bay, and Okonjeje rocks.

Presumably the reason why certain intrusions, dominantly tholeiitic, show absolute enrichment in iron is to be found in the changing chemistry and variable position in the crystallization sequence of the iron ores, a reflection of oxidation-reduction equilibria prevailing during crystallization. The state of oxidation of the iron is directly controlled by the

concentration or pressure of water in the melt, high [H_2O] resulting in a high Fe_2O_3/FeO ratio. Hence analcime-bearing alkali olivine-basalt hypabyssal rocks, reflecting in their mineralogy a 'wet' magmatic parentage, would not be expected to reveal absolute iron enrichment to any great extent.

If crystallization of basic magma takes place initially under reducing conditions, most of the iron is present as FeO. Goldschmidt (1954, p. 38) has drawn attention to the primitive reduced state of the Skaergaard chilled marginal facies. A specimen (J5) from one of the feeder dykes to the Black Jack sill, collected from colliery workings below the main intrusion, has the lowest Fe_2O_3/FeO ratio (0·24) of any of the teschenites, despite slight modification by residual solutions. This rock completed its crystallization before the magma entered the final magma chamber, after which oxidizing conditions became increasingly more effective.

In the early and middle stages of differentiation of basic magma the iron, principally in the ferrous state, enters the ferro-magnesian silicates, which, with falling temperature, become progressively enriched in iron relative to magnesia. If Fe_2O_3 is low in the early stages, the amount of ore precipitated is very slight; the Skaergaard marginal facies contains 0·5 to 1·0 % ore. Under continued reducing conditions very little FeO is lost as ore in the early and middle stages of differentiation, for the ore consists predominantly of Fe_3O_4–Fe_2TiO_4 solid solutions. The amount of titanomagnetite precipitated depends on the available Fe_2O_3. Whilst more data on the titanomagnetites from more primitive basic representatives is desirable, present information on such minerals would suggest that the quantity of Fe_2TiO_4 entering into solid solution does not exceed 50 %. Indirectly, then, the amount of Fe_2O_3 available at this stage for ore formation tends to control the quantity of FeO and TiO_2 lost to magma as precipitated ore.

Under continued reducing conditions, FeO (and to a lesser extent TiO_2) may be continually concentrated in successive magmatic fractions. The olivine may then attain compositions in the vicinity of Fa_{90-95}; tholeiitic pyroxenes also show strong iron enrichment. If the Black Jack magma had not undergone progressive oxidation in the final magma chamber, it is probable that olivine compositions up to nearly pure fayalite[1] would have been encountered, while the composition of the most iron-rich analysed clinopyroxene ($Ca_{47}Mg_{33}Fe_{20}$) would have moved farther towards hedenbergite.

[1] The most iron-rich olivine has a composition of Fa_{60}.

If oxidation processes are effective in the early and middle stages of differentiation, much of the excess iron over that necessary for the ferro-magnesian silicates is dissipated as ore, which may show an even distribution throughout the rock series, or, as is often the case, actually increase in amount in the middle and later stages of evolution. In the Black Jack sill the amount of modal iron ore decreases slightly at first in the lower teschenites. In the teschenites occurring at elevations greater than 250 to 300 feet above the lower contacts the amount of modal iron ore increases.

In hypabyssal basic rocks the stage of maximum iron enrichment following earlier conditions of slight oxidation is exemplified by the ore-enriched tholeiitic dolerite pegmatites, whose consolidation occurred when volatile (oxidizing) conditions became important (Walker, 1953). These rocks in certain instances contain up to 18 % total iron, a large proportion of which is in the ferric state.

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An X-ray investigation of some rare-earth silicates: cerite, lessingite, beckelite, britholite, and stillwellite.

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Summary. An X-ray study of a number of rare-earth silicates has been carried out; single-crystal and powder data are presented.

It is found that cerites can contain up to at least 6 % CaO without disruption of the structure, which is trigonal with probable space-group $P321$ &c. The cell dimensions are a ca. 10·8 Å., c ca. 37–38 Å., although there is a strong pseudo-cell with a halved c-axis. An ideal formula $(Ca,Ln\dagger)_3Si_2(O,OH,F)_9$ is proposed for this series.

Lessingite and beckelite can be regarded chemically as lime-rich members of this cerite series. They do not, however, have the same crystal structure as cerite; their diffraction patterns are very similar to that of britholite, and indicate a structure dimensionally comparable with apatite. For a hexagonal cell, the dimensions are a ca. 9·7 Å., c ca. 7·1 Å., with probable space-group $P6_3$, &c. An ideal formula $(Ca,Ln)_2(Si,Al,P)(O,OH,F)_5$ is proposed for this series. Marked biaxial optical properties suggest that the structure may be truly orthorhombic, with a very close dimensional approximation to a hexagonal cell.

The new mineral, stillwellite, is unrelated to either of these series. It is trigonal with cell dimensions a ca. 6·9 Å., c ca. 6·7 Å., with probable space-group $P3_112$. An ideal formula $(Ca,Ln)(Si,Al,P)B(O,OH,F)_5$ suggested by previous work is confirmed.

THERE are many rare-earth silicates described in the literature. Usually they are of isolated occurrence, and the descriptions by which they are characterized are not very satisfactory. Often the minerals are poorly crystallized, and this, taken with the fact that their refractive indices are usually quite high (1·75 to 1·85), makes an accurate optical definition difficult. This may be the reason why, for some specimens, different investigators have reported different optics, although it is more probable that this is owing to variable optical properties, arising from complex solid solution. Complete separation of the mineral from the rock has not always been possible; together with difficulties in the chemical analysis this leads to uncertainties in the formulae that have been proposed for many of the minerals. Thus, with the properties and constitutions of most of these silicates very imperfectly known, it is difficult to see what, if any, are the relationships between them.

† The symbol Ln is used throughout this paper as an inclusive symbol for the rare-earth elements or lanthanons, Yt,La,Ce,...,Lu.

The work to be described in this paper was begun with an investigation of a new mineral, stillwellite. Further work on the other minerals was then undertaken in order that they might be compared both with stillwellite and among themselves. The X-ray investigation has been carried out by conventional methods. Single-crystal photographs have been used, in the main, to obtain the cell dimensions and space-group data. These have been used with the chemical analyses to calculate the cell contents and to attempt to derive formulae for the minerals. Where sufficient of the material was available, powder data have been obtained, usually by Geiger-counter diffractometer methods. Other comments upon the methods employed will be made where appropriate.

Cerite.

Cerite occurs as a red-brown mineral usually in the massive form; two of the best known localities are Bastnäs, Sweden, and Jamestown, Colorado, U.S.A. Measurements by Nordenskiöld on a rare well-formed crystal (Hintze, 1897) suggest that the mineral is orthorhombic (pseudo-tetragonal) with $a:b:c::0{\cdot}9988:1:0{\cdot}8127$. There appears to be no analysis of the material from which this crystal was taken, although a number of other analyses of cerites from the same locality are given in Hintze. From these a formula $(Ca,Fe)_2Ln_2Si_6O_{26}H_6$ has been proposed. The optical properties are slightly variable with refractive indices ca. 1·81–1·82 and a low positive birefringence; the mineral also shows a feeble pleochroism.

X-ray investigation. A number of single-crystal specimens both from Swedish and American localities were used. It was soon established that the symmetry is trigonal, with Laue group $\bar{3}m$. The cell dimensions were found to be a ca. 10·8 Å., c ca. 37–38Å., though there is a strong pseudo-cell with c ca. 18·5–19 Å. The true unit cell is disclosed by a small number very weak reflections midway between the strong 19 Å. layer-lines on c-axis oscillation photographs; for some specimens, these may be missed if the exposure time is too short. If these weak reflections are ignored the pseudo-cell is rhombohedral with space-group $R32$, $R3m$ or $R\bar{3}m$. If these weak reflections are included it is seen that the true unit cell is hexagonal with space-group probably $P321$, $P3m1$, or $P\bar{3}m1$, &c. The space-groups $P3_112$, &c. cannot be ruled out, for although a careful examination of the $000l$ reflections has been made no contradiction of the conditions $000l$ ($l = 3n$) has been found. These absences, however, may well be accidental, for such reflections are al-

due to the true cell with the doubled c-axis; the strongest true cell reflection observed is very weak. Piezo-electric tests have provided no positive evidence.

Accurate cell dimensions were obtained for several specimens, using a back-reflection camera (dimensions in Å.):

63425 Bastnäs, Sweden	a 10·81±0·02	c 37·72±0·05	c/a 3·489
53116 „ „	10·82±0·02	37·71±0·05	3·485
63431 Jamestown, Colorado, U.S.A.	10·73±0·02	37·70±0·05	3·514

Specimens from Mountain Pass, California, and Swedish specimens accepted by Nordenskiöld as cerite were also examined. Single crystals from the Californian specimen were of poor quality; although it was possible to confirm that the diffraction pattern was similar to that of other cerites, no dimensional data were obtained. Examination of the Nordenskiöld material showed that it was identical with other Swedish cerites, and no further work was carried out on it.

Besides the small but significant difference in the a cell side in the American cerite, another important difference is in the intensities of the weak true cell reflections. These reflections are about twice as strong for the Jamestown cerite.

It is difficult to obtain satisfactory powder data for cerite. In common with other rare-earth silicates, there is some fluorescence with Cu-$K\alpha$ radiation; this is presumably due to the L absorption edges of the rare earths, which in the case of lanthanum go up to 2·254 Å. The quality of the lines on the powder diagrams is poor, probably owing to a partial disruption of the crystal structure towards the metamict state by some radioactive atoms within the crystal. A considerable sharpening of the powder lines may be obtained by heating the specimen for 1 to 2 hours at 800 to 900° C. For cerite in particular the powder pattern is complex, consisting of a large number of relatively weak lines.

Table I presents the results of powder records from a specimen of cerite (53116) heated for 1 hour at 900° C. This table shows a combined spacing list both from diffractometer records (with Cu-$K\alpha$ radiation and a Si standard) and photographic measurements (Cr-$K\alpha$ radiation); some of the weaker peaks are lost in the relatively high background of the diffractometer record. The spacings of some planes calculated from the single-crystal cell dimensions are also shown for the first thirteen lines; the indexing refers to the pseudo-cell since no true-cell reflections will be strong enough to be observed on the powder record. The agreement between the calculated and observed spacings is not good but it can be

regarded as satisfactory in the light of the difficulties of measurement. The strongest lines are at 2·93, 2·66, and 1·93 Å.

Chemical analysis. A sample of cerite (53116) was prepared for analysis by crushing and passing through a 90-mesh sieve; after washing with

TABLE I. Powder data for cerite (53116) after heating for 1 hour at 900° C.

$d_{obs.}$	I	*hkil.*	$d_{calc.}$	$d_{obs.}$	I	$d_{obs.}$	I
8·53*Å.	vw	$1\bar{1}01$	8·39	2·26*	vvw	1·523*	vvw
6·75*	vvw	$10\bar{1}2$	6·65	2·19	vw	1·503*	vvw
6·39*	vvw	0003	6·29	2·13*	vvw	1·470*	vvw
5·32	vw	$11\bar{2}0$	5·41	2·09	vw(b)	1·426*	vvw
4·50	w	$20\bar{2}1$	4·55	2·06	vw(b)	1·414*	vvw
4·20	vw	$2\bar{2}02$	4·20	2·03	vvw	1·374*	vvw
		$1\bar{1}04$	4·21	1·98	vvw	1·357*	vvw
3·50	w	$21\bar{3}1$	3·50	1·96	w	1·336*	vvw
3·45	mw	$10\bar{1}5$	3·48	1·93	mw(b)	1·297*	vvw
3·33	vvw	$20\bar{2}4$	3·32	1·843	vw	1·289*	vvw
3·28	w	$21\bar{3}2$	3·32	1·831	vw	1·265*	vvw
3·10	w	0006	3·14	1·804	vvw	1·256*	vvw
		$30\bar{3}0$	3·12	1·751	vw	1·242*	vvw
2·93	m	$2\bar{2}05$	2·94	1·729	vw	1·224*	vvw
2·80	vw	$2\bar{3}14$	2·83	1·683*	vvw	1·206*	vvw
		$30\bar{3}3$	2·80	1·658	vvw	1·175*	vvw
2·73	vw	—	—	1·635	vvw	1·166*	vvw
2·66	mw	—	—	1·590*	vvw	—	—
2·55	vw	—	—	1·572	vvw	—	—
2·28*	vvw	—	—	—	—	—	—

For the first thirteen lines the spacing has been calculated from the dimension of the pseudo-cell determined by single-crystal methods. (*) indicates that th line was observed only on the photograph taken with Cr-$K\alpha$ radiation; all othe spacings were observed both on the photographs and the diffractometer record obtained with Cu-$K\alpha$ radiation.

water, a concentrate of cerite was obtained by magnetic separation. The fraction of this concentrate which passed through a 200-mesh sieve was further purified by centrifuging with Clerici solution, the lighter portion being rejected. The separation and analysis were carried out by J. H. Scoon.

The analysis showed 0·30 % CO_2, presumably owing to bastnäsite ($LnFCO_3$) that could not be separated from the cerite. The analysis after correction for bastnäsite is shown in table II together with other analyses of cerites.

The present analysis compares quite well with those of Nordström and of Goddard and Glass. As pointed out by Goddard and Glass, the Colorado cerite differs from the Swedish material principally in having a higher CaO content; the 4·35 % CaO in the analysis by Nordström

higher than the usual lime content in analyses of Swedish material. The fourth analysis, by Hanson and Pearce, is remarkably different from the other three; there are major discrepancies in Al_2O_3 and CaO.

Contents of the unit cell. The density of the analysed sample was 4·89,

TABLE II. Chemical analyses of cerite.

	1.	2.	3.	4.	5.
SiO_2	21·24	21·24	22·79	18·10	17·42
Al_2O_3	nil	nil	1·26	0·32	14·59
Fe_2O_3	0·43	0·43	—	—	—
FeO	0·68	0·68	3·92	1·54	1·40
TiO_2	nil	nil	—	—	—
MnO	nil	nil	—	0·22	0·40
MgO	1·88	1·88	—	0·21	1·68
Ce_2O_3	31·37	30·91	24·06	32·97	21·65
ThO_2	nil	nil	—	—	—
La_2O_3, &c.	33·37	32·76	} 35·37	35·72	} 27·55
Yt_2O_3, &c.	5·27	5·18		3·86	
CaO	2·97	2·97	4·35	5·80	15·24
H_2O+	2·00	2·00	3·44	1·26	0·07
H_2O-	0·10	0·10	—	—	—
F	1·47	1·36	—	—	—
CO_2	0·30	—	—	—	—
	101·08	99·51			
$O \equiv F$	0·62	0·57	—	—	—
Total	100·46	98·94	99·52	100·00	100·00

1. Cerite (53116), Bastnäs, Sweden, this investigation. Material includes some allanite and bastnäsite. Analyst, J. H. Scoon.

2. Analysis of cerite (53116) (col. 1) after correction for bastnäsite, assuming all the CO_2 is present as bastnäsite.

3. Cerite, Sweden. Total includes 4·33 % extraneous material. Analysis by Nordström, quoted in Hintze (1897).

4. Cerite, Jamestown, Colorado, U.S.A. (Goddard and Glass, 1940). Recalculated analysis after correction of cerite rock analysis for 0·86 % uraninite, 5·00 % bastnäsite, 5·00 % quartz, and 11·32 % fluorite. Analyst, J. G. Fairchild.

5. Cerite, Jamestown, Colorado, U.S.A. (Hanson and Pearce, 1941). Analysis recalculated from cerite rock analysis.

in good agreement with previous density determinations. On the basis of this and the X-ray data, the cell contents may be calculated as: (Ca,Ln,Fe^{2+},Fe^{3+},Mg) 61·52, Si 40·36, total anions 185·62.

Z may then be taken as either 20 or 21, which yield a formula

$$(Ca,Ln)_{3\cdot08}Si_{2\cdot02}(O,OH,F)_{9\cdot28} \quad \text{or} \quad (Ca,Ln)_{2\cdot93}Si_{1\cdot92}(O,OH,F)_{8\cdot84};$$

thus the ideal formula of this cerite must be regarded as

$$(Ca,Ln)_3Si_2(O,OH,F)_9.$$

The large cell dimensions make it difficult to determine *Z* unambiguously.

Discussion. From the above results it is established that the North American and Swedish cerites are structurally similar and that they have trigonal symmetry.[1] It seems probable, therefore, that the early goniometrical measurements were carried out on some other mineral. A chemical formula for the Bastnäs cerite has been established; this is very similar to that previously proposed, which is usually written in the form $(Ca,Fe)O:1\frac{1}{2}Ln_2O_3:3SiO_2:1\frac{1}{2}H_2O$. On the basis of their work Goddard and Glass proposed a series with increasing CaO content of the cerite, from a hypothetical CaO-free cerite, $2Ln_2O_3:3SiO_2:H_2O$ through the intermediate cerite from Colorado, $CaO:2Ln_2O_3:3SiO_2:H_2O$ to a CaO-rich variety described as lessingite, $2CaO:2Ln_2O_3:3SiO_2:H_2O$.

Swedish cerites may be regarded as intermediate in this series between the CaO-free and Colorado cerites. The chemical constitution proposed by Hanson and Pearce for the Colorado cerite does not fit into this series and is unrelated to that of the Swedish varieties; the inclusion of water in the formula is also disputed by these authors. The present work supports the suggestion that a series of cerites with variable lime content exists. The close structural similarity between the Swedish and American varieties, and the agreement between the present analysis and that of Goddard and Glass, show that the work of Hanson and Pearce must be rejected.

It is noteworthy that the ratio of the CaO contents in the Jamestown and Bastnäs materials is roughly the same as the ratio of the intensities of the weak true cell reflections. Thus it is thought that the hypothetical CaO-free cerite will be truly rhombohedral; the addition of lime forms a hexagonal superstructure, which becomes more pronounced with increasing lime content. To what extent this CaO content can be increased before the cerite structure is disrupted will become clear after the descriptions of the examinations of lessingite and beckelite $(3CaO.2Ln_2O_3.3SiO_2)$.

Lessingite, beckelite, and britholite.

It is convenient to discuss these three minerals together since they are very similar.

Lessingite was described by Zilbermintz (1929) from the Kyshtym district of the Urals, Russia. It is a red-brown mineral with refractive

[1] In a recent note (Glass, Evans, Carron, and Rose, 1956) cerite from Mountain Pass, California, was incorrectly described as monoclinic. The relationship of this 'monoclinic cell' to the trigonal cell has been discussed in detail elsewhere (Gay 1957).

indices ca. 1·78–1·79 and low negative birefringence (0·006); it is biaxial with $2V_\alpha$ ca. 44°. The density was 4·69, and a formula $Ca_2Ln_4Si_3O_{15}H_2$ was suggested on the basis of a chemical analysis. It could therefore be considered a calcic member of the cerite series.

Beckelite was described by Morozewicz (1905, 1930) as large crystals occurring in mariupolite from the Sea of Azov, Russia. The yellow-brown material was thought to be cubic, although large crystals show weak birefringence; the refractive index is ca. 1·81. The density was 4·15, and chemical analysis suggests a formula $Ca_3Ln_4Si_3O_{15}$. It has been regarded as a member of the pyrochlore family, but it seems more likely that it is to be regarded as a lime-rich member of the cerite family.

Britholite was first described by Winther (1901) as phenocrysts in pegmatite from Naujakasik, Greenland. The brown mineral is said to be orthorhombic (pseudo-hexagonal by twinning on {110}) with $a:b:c$ :: 0·620 : 1 : 0·423; large crystals sometimes show a sectored development. The mineral has a low negative birefringence and small $2V_\alpha$; according to Barth and Berman (1930) its refractive index is about 1·77–1·78. The density was 4·45, and the formula $(Ca,Ln)_5(Si,P)_3(O,OH,F)_{13}$ has been suggested. Bøggild (1912) disputed the orthorhombic character of the mineral and regarded it as uniaxial with optical anomalies. X-ray measurements by Hägele and Machatschki (1939) showed a hexagonal cell with a 9·61, c 7·02 Å.; these authors also suggested that britholite belonged to the apatite group.

X-ray investigation. Single crystals of the three minerals were obtained from rock specimens from the type localities. For lessingite and britholite there was no difficulty in identifying the minerals. The beckelite crystals, however, were only obtained after a number of sections of mariupolite had been examined; in these, large crystals that seemed to conform to the earlier incomplete description of the mineral were located; the material for the X-ray work was then obtained from the large phenocrysts in the rock specimens that matched the grains located in the corresponding section. Probably this material is identical with beckelite as defined by Morozewicz.

The three minerals give very similar diffraction patterns. Laue photographs established an apparent hexagonal symmetry, with probable Laue group 6/*mmm*. Single-crystal studies, however, revealed intensity discrepancies between corresponding reflections. For these minerals a reliable comparison of intensities is difficult owing to the relatively high absorption and fluorescence with Cu-$K\alpha$ radiation. If allowance is made for these effects, it seems probable that the true

Laue symmetry is $6/m$, although the possibility that the crystals are only dimensionally hexagonal cannot be completely discounted (see later). Taking the symmetry to be hexagonal, $000l$ reflections are present only when $l = 2n$, suggesting a probable space-group $P6_3$ or $P6_3/m$. Piezo-electric tests provided no positive evidence.

TABLE III. Powder data for lessingite.

$d_{obs.}$	I	$hkil$	$d_{calc.}$	$d_{obs.}$	I	$hkil$	$d_{calc.}$
4·72 Å.	vw	$11\bar{2}0$	4·83	2·019	vvw	$40\bar{4}1$	2·007
4·19	vw	$20\bar{2}0$	4·19	1·995	w	$22\bar{4}2$	1·996
3·99	w	$11\bar{2}1$	3·99	1·941	vw	$31\bar{4}2$	1·941
3·58	w	$20\bar{2}1$	3·60	1·894	w	$33\bar{6}1$	1·901
3·54	w	0002	3·54	1·890	w	$21\bar{3}3$	1·891
3·34*	vw	—	—	1·855	vw	$32\bar{5}1$	1·854
3·26	w	$10\bar{1}2$	3·26	1·827	vw	$41\bar{5}0$	1·827
3·16	mw	$21\bar{3}0$	3·16	1·802	w	$40\bar{4}2$	1·802
2·89	s	$21\bar{3}1$	2·89			$30\bar{3}3$	1·801
2·86	m	$11\bar{2}2$	2·86	1·769	vvw	0004	1·770
2·79	mw	$30\bar{3}0$	2·79			$41\bar{5}1$	1·769
2·32	vvw	$31\bar{4}0$	2·32	1·577	vvw	—	—
2·25	vvw	$10\bar{1}3$	2·27	1·547	vvw	—	—
2·12	vw	$11\bar{2}3$	2·19	1·516	vvw	—	—
2·10	vvw	$40\bar{4}0$	2·09	1·495	vvw	—	—
2·05	vvw	$20\bar{2}3$	2·05	1·470	vvw	—	—
				1·271	vvw	—	—
				1·255	vvw	—	—

* This reflection could not be indexed on the basis of the single-crystal cell dimensions, and is probably due to impurity.

The following cell dimensions were found using single-crystal back-reflection methods:

Lessingite	a 9·67±0·02 Å.	c 7·08±0·02 Å.	c/a 0·732
Beckelite	9·66±0·02	7·07±0·02	0·732
Britholite	9·61±0·02	7·03±0·02	0·731

There are only very slight differences between the three minerals.

A powder pattern was obtained for lessingite; suitable material was not available for the other two minerals. The diffractometer record with Cu-$K\alpha$ radiation is of the same quality as those for the other rare-earth silicates examined. Measurements of line spacings are listed in table III together with the calculated spacings of certain planes obtained from the single-crystal data; there is satisfactory agreement between the observed and calculated spacings. It is reasonable to assume that the powder patterns of beckelite and britholite will be very similar to that of lessingite, with some small changes in line positions and intensities. For lessingite the strongest lines are at 2·89, 2·86, and 2·79 and 3·16 Å.

Chemical analyses. In view of the limited amount of the minerals available, it was not possible to undertake any new chemical analyses. Since, however, there are close similarities in the structural arrangements, it is of interest to compare the three published analyses; these are given in table IV. They show a correlation that is particularly marked for lessingite and britholite if allowance is made for the replacement of Si by P.

TABLE IV. Chemical analyses of lessingite, beckelite, and britholite.

	1.	2.	3.
SiO_2	19·85	17·13	16·77
P_2O_5	1·13	—	6·48
Al_2O_3	0·26	0·30	—
ZrO_2	—	2·50	—
Fe_2O_3	0·65	—	0·43
Mn_2O_3	—	0·07	—
Ce_2O_3, &c.	22·48	28·10	
La_2O_3, &c.	36·65	31·60	60·54
Yt_2O_3, &c.	3·42	2·86	
MnO	0·88	—	—
MgO	0·17	—	0·13
CaO	11·71	15·46	11·28
K_2O	0·08	0·39	—
Na_2O		0·78	1·85
H_2O^+	1·56	0·99	1·27
H_2O^-	0·38	—	—
F	0·54	—	1·33
CO_2	0·35	—	—
	100·11	100·18	100·08

1. Lessingite, Kyshtym district, Urals, Russia (Zilbermintz, 1929).
2. Beckelite, Mariupol, Sea of Azov, Russia (Morozewicz, 1905).
3. Britholite, Naujakasik, Julianehaab, Greenland (Winther, 1901).

Contents of the unit cell. By using the analyses and densities quoted above, together with the determined cell dimensions, the contents of the unit cells may be calculated:

	Lessingite	Beckelite	Britholite
Ca, Ln, Fe, &c.:	10·32	9·78	9·67
Si, Al, P, &c.	5·72	4·44	5·63
Total anions:	26·87	21·84	25·61

If $Z = 5$ the formulae are: Lessingite $(Ca,Ln)_{2\cdot06}(Si,Al,P)_{1\cdot14}(O,OH,F)_{5\cdot37}$; beckelite $(Ca,Ln)_{1\cdot96}(Si,Al,Zr)_{0\cdot89}(O,OH)_{4\cdot37}$; britholite $(Ca,Ln)_{1\cdot94}(Si,P)_{1\cdot13}(O,OH,F)_{5\cdot12}$.

It is to be expected that the cell contents would be approximately the same for all three minerals. It is probable that the lessingite should be

corrected for a small amount of bastnäsite impurity (0·35 % CO_2); when this is done, there is good agreement between lessingite and britholite. As expected, the beckelite cell-contents are not satisfactory; in the absence of new data, it is not possible to say whether this is owing to errors in the analysis or density (which is rather low for these minerals). If Z is chosen as 5, the best structural formulae given in the table are obtained; the idealized structural formula for this series appears to be $(Ca,Ln)_2(Si,Al,P)(O,OH,F)_5$.

Discussion. From the evidence given above, it must be concluded that lessingite, beckelite, and britholite are very similar. They are based upon the same crystal structure, which appears to be dimensionally similar to apatite. Complex replacement can occur within the structure, leading to the differences in optical properties by which the minerals have been distinguished. The basic structure is different from that of the cerite series, showing that the cerite structure is disrupted by too large a proportion of Ca ions.

The results given above have been calculated upon the hypothesis that the crystals have hexagonal symmetry. Within the limits of the experimental accuracy, the minerals are dimensionally hexagonal; the orthorhombic axial ratios given by Winther (1901) for britholite would certainly have been detected. Nevertheless, some doubts as to the true symmetry are raised by the optical properties; both britholite and lessingite have been described as biaxial, and an examination of beckelite shows some biaxial character. Some optical work upon the present specimens has been carried out by Drs. I. D. Muir and J. D. C. McConnell. They have shown that beckelite and britholite are similar in that they have substantially the same refractive indices with a small optic axial angle. Such discrepancies might well be attributed to anomalous uniaxial behaviour; but the examination of lessingite confirmed that the optic axial angle was large ($2V_\alpha$ ca. 35°) and it seems unlikely that this can be explained as an anomalous property.

To resolve these doubts and establish the true symmetry of these minerals would require the accurate measurement of the intensities of reflections from planes of related indices. As has been pointed out earlier this is very difficult to carry out, for the minerals have high absorption and fluoresce with Cu-$K\alpha$ radiation. The problem of the absorption could be overcome by the use of Mo-$K\alpha$ radiation but unfortunately this still causes some fluorescence. No further work has been carried out on this point at the moment.

Stillwellite.

Stillwellite, a new mineral from the Mary Kathleen lease, N.W. Queensland, has been described by McAndrew and Scott (1955). In a preliminary report they describe the mineral as trigonal with a 6·85 Å., c 6·64 Å., and space-group[1] $P3m$, $P\bar{3}m$, or $P3_n2$. The density was 4·57; on the basis of this and a preliminary analysis, an ideal formula (Ln,Ca) B(Si,P)(O,OH,F)$_5$ with $Z = 3$ was suggested. The mineral, which is colourless in thin section, shows slightly variable optics with moderate birefringence, the refractive indices being about 1·78.

An examination of the mineral from the same locality had been commenced before the preliminary report described above was published. The more detailed X-ray and chemical examination will be described below.

X-ray investigation. The Laue group was established as $\bar{3}m$. Single-crystal oscillation and Weissenberg photographs showed that the lattice is hexagonal, and 000l reflections are present only if $l = 3n$, suggesting a space-group of the type $P3_112$, &c. In view of the ambiguities in the space-groups reported above, a further investigation was made to seek the absent reflections using both Cu-$K\alpha$ radiation and Mo-$K\alpha$ radiation, but none was found. For this material it seems unlikely that all orders could be fortuitously absent, and thus it must be concluded that the probable space-group is $P3_112$, &c. Piezo-electric tests provide no positive evidence.

Cell dimensions determined from single-crystal back-reflection photographs are a 6·89±0·03 Å., c 6·70±0·02 Å., c/a 0·972. These agree with those determined by McAndrew and Scott.

Powder data for stillwellite have been obtained from powder diffractometer records using Cu-$K\alpha$ radiation. Difficulties similar to those described earlier for cerite had to be overcome before a satisfactory pattern could be obtained. The spacings are listed in table V, together with the spacings of a number of planes calculated from the single-crystal cell dimensions; the agreement is satisfactory. There are a few weak lines that cannot be indexed, which are probably due to apatite inclusions (see later). The strongest lines are at 2·96 Å., 3·43 Å., and 2·91 Å.

Chemical analysis. A sample of stillwellite (77991) for analysis was prepared in the manner described earlier for cerite. A small amount of apatite and uraninite could not be removed; a correction for the

[1] The symbol $P3_n2$ was used to imply the space-groups $P32$ and $P3_112$, &c.

apatite was applied by carrying out a partial analysis of a sample from which the apatite had been removed by cold nitric acid. The separation and analyses were carried out by J. H. Scoon and the results are shown in table VI. When compared with the preliminary analysis of McAndrew and Scott, it is seen that there is good agreement if allowance for apatite is made in the earlier work.

TABLE V. Powder data for stillwellite (77991) after heating for 2 hours at 900° C.

$d_{obs.}$ Å.	I	$hkil.$	$d_{calc.}$	$d_{obs.}$ Å.	$I.$	$hkil.$	d_{calc}
5·96	vvw	$10\bar{1}0$	5·97	1·785	vw	$20\bar{2}3$	1·788
4·44	m	$10\bar{1}1$	4·46	1·704	w(b)	$22\bar{4}0$	1·723
3·43	s	$11\bar{2}0$	3·44			$30\bar{3}2$	1·710
3·13*	w	—	—	1·646	mw(b)	$22\bar{4}1$	1·668
3·05	w	$11\bar{2}1$	3·06			$31\bar{4}0$	1·655
2·96	s	$20\bar{2}0$	2·98	1·612	vw	$10\bar{1}4$	1·612
2·79*	vw	—	—			$31\bar{4}1$	1·606
2·71	mw	$20\bar{2}1$	2·73	1·526	vw(b)	—	—
2·40	w	$11\bar{2}2$	2·40	1·476	vvw	—	—
2·24	mw	$21\bar{3}0$	2·25	1·458	vvw	—	—
2·23	mw	0003	2·23	1·448	vvw	—	—
		$20\bar{2}2$	2·23	1·357	vw	—	—
2·13	ms	$21\bar{3}1$	2·14	1·341	vw	—	—
2·09	vvw	$10\bar{1}3$	2·09	1·335	w	—	—
1·979	vw	$30\bar{3}0$	1·989	1·324	vvw(b)	—	—
1·935*	w	—	—	1·259	vw	—	—
1·896	w	$30\bar{3}1$	1·906	1·205	vw	—	—
1·864	m	$11\bar{2}3$	1·874	1·185	vvw	—	—
		$21\bar{3}2$	1·871	1·118	vvw	—	—

* These reflections could not be indexed on the basis of the single-crystal cell dimensions, and are probably due to apatite inclusions that could not be separated from the stillwellite. Fluorapatite has relatively strong reflections for spacings of 2·78 Å. and 1·933 Å.; there is also a weak line at 3·16 Å., which may account for that observed at 3·13 Å.

Contents of the unit cell. The density of the analysed sample was 4·58. On the basis of this and the X-ray data the cell contents are: Ca, Ln, &c., 3·04; Si, Al, P, 2·98; B, 2·66; total anions 14·88.

If Z is taken as 3, the formula becomes $(Ca,Ln)_{1\cdot01}(Si,Al,P)_{0\cdot99}B_{0\cdot89}(O,OH,F)_{4\cdot96}$; thus the ideal formula must be regarded as $(Ca,Ln)(Si,Al,P)B(O,OH,F)_5$.

Discussion. Stillwellite shows no simple relationship to cerite and related minerals. It may be distinguished from them both by optical and X-ray methods. It may be compared with another boron-bearing rare-earth silicate, melanocerite, of which, unfortunately, no specimen was available for investigation.

TABLE VI. Chemical analyses of stillwellite.

	1.	1*a*.	2.	3.
SiO_2	21·46	22·30	22·40	20·1
P_2O_5	1·93	0·64	0·67	2·58
Al_2O_3	0·40	—	0·42	—
Fe_2O_3	0·17	—	0·18	—
MgO	0·06	—	0·06	—
CaO	2·65	0·91	0·95	3·96
Ce_2O_3	31·87	61·50	33·15	58·4
La_2O_3, &c.	26·80		27·95	
Yt_2O_3, &c.	0·71		0·74	
B_2O_3	11·73	—	12·23	11·5
H_2O^+	0·81	—	0·85	—
H_2O^-	0·10	—	0·10	—
F	0·40	—	0·30	—
U_3O_8	0·67	—	—	—
ThO_2	0·06	—	—	—
	99·82			
$O \equiv F$	0·17			
Total	99·65		100·00	

1. Stillwellite (77991) in stillwellite–garnet–allanite skarn, Mary Kathleen leases, Mt. Isa district, Queensland, Australia. The material contains apatite and uraninite inclusions. Analyst, J. H. Scoon.

1a. Partial analysis of stillwellite with apatite removed by HNO_3 extraction. The figure for the rare earth oxides is wt. % with cerium as CeO_2.

2. Analysis in column 1 recalculated to 100 after removal of uraninite and enough CaO, P_2O_5, and F to reduce the values of CaO and P_2O_5 to these shown in column 1*a* for the apatite-free material.

3. Results of preliminary analysis published by McAndrew and Scott (1955).

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A contribution to the mineralogy of chloritoid.

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Summary Chloritoids from the Saxa Vord schists in the Shetland Isles and the Dalradian schists north of Stonehaven have been studied optically and chemically. In both cases monoclinic and triclinic crystals occur with $\alpha = b$ in the monoclinic varieties. Twinning is common with twin axes [110] and [230]. The formula of chloritoid is considered in relation to the structure recently suggested by Brindley and Harrison (1952).

CHLORITOID has been recorded from several localities within the United Kingdom. It is well developed in the Shetland Isles, and in Scotland along a narrow belt of ground nearly 22 miles long extending from the coast north of Stonehaven to the valley of the North Esk. In England it has been recorded from the Tintagel area.

The present study is concerned with chloritoid occurring in the Saxa Vord Schists of Unst in the Shetland Isles (Read, 1934), and in the Dalradian Schists north of Stonehaven (Barrow, 1898; Harker, 1939; Williamson, 1953).

Occurrence and petrology. The geology of Unst has been described by Read (1934). He has shown that the island consists of several blocks separated by steep thrusts, the Saxa Vord schists forming part of the Saxa Vord block in the north of the island. The metamorphic history of these schists is as follows (Read, 1934): an early metamorphic phase resulted in the formation of andalusite-staurolite schists; this was followed by a retrogressive metamorphism, which gave rise to the now dominant chloritoid-kyanite schists. Later, thrusting resulted in the development of chlorite-muscovite schists around the margin of the block. Relict grains of staurolite are common in the chloritoid schists whilst andalusite has been pseudomorphed by sericite and kyanite; garnet, which is poorly developed, was considered by Read to have been coeval with andalusite and staurolite. The present study has shown that garnet formed after chloritoid, indicating that the chloritoid-producing retrogressive metamorphic phase was followed by a progressive phase (Snelling, 1954). The chloritoid occurs as rectangular

porphyroblasts about 1 mm. in length with random orientation. Although flakes of this mineral commonly grow on staurolite grains the direct replacement of staurolite by chloritoid has not been observed. Inclusions are remarkably few, consisting mainly of magnetite and occasionally quartz. The analysed chloritoid was separated with some difficulty, and a complete separation from the fine-grained muscovite that forms the groundmass of these schists proved impossible. However, an attempt has been made to correct the analysis for this impurity.

In the coast section between Stonehaven and Aberdeen, chloritoid first occurs about half a mile north of the Highland Border Fault. Anderson (1942) considers that the Dalradian in this section consists essentially of a psammitic group composed of quartzites and schistose grits, and an older pelitic group of mica schists with biotite, chloritoid, or staurolite, depending on the degree of metamorphism. He suggested that the psammites occur in synclines and tentatively correlated them with the Ben Ledi grits, whilst the pelites were correlated with the Pitlochry schists.[1] The chloritoid schists from this area are much coarser in grain size than the Saxa Vord schists. Chloritoid occurs as prominent porphyroblasts often 5 mm. in length. In thin section they are extremely ragged and riddled with quartz inclusions. Alteration is common, both chloritoid and chlorite being replaced by a mixture of kaolinite, chalybite, and limonite. The characteristic mineral assemblage is chloritoid, chlorite, and muscovite. Biotite is absent and garnet only occasionally found, though the rocks lie well within the garnet zone of Barrow (1912). Because of the numerous quartz inclusions the separation of a pure sample of chloritoid was impossible, but an attempt has been made to correct the analysis for the excess of silica and is discussed below.

Analyses of the schists from which the two chloritoids were separated are given in table I. The most noticeable difference between the two rocks is the higher Niggli *mg* value of the Stonehaven schist, probably reflecting the high chlorite content of these rocks.

Optical properties. Both analysed chloritoids show the usual pleochroic scheme, with α = green, β = slate blue, and γ = pale yellow; other optical properties are (α, β, and γ $\pm 0{\cdot}003$; $2V \pm 2°$):

Stonehaven	α 1·721	β 1·725	γ 1·728	$\gamma-\alpha$ 0·007	$2V_\gamma$ 55°
Unst	1·716	1·719	1·724	0·008	56°.

[1] Several other chloritoid localities were mapped by Barrow (1898) between this section and Glen Esk, all occurring in the Dalradian within a mile or so of the

Most of the grains are twinned, and in view of the recent study by Hietanen (1951) the optic orientations of the chloritoids from both localities have been studied in some detail. Repeated twinning is rare, binary and ternary twins being most common; in all cases the composition plane of the twin lamellae is parallel to the basal cleavage. In the determination of the twin laws the cell dimensions determined by Milne (1949) and confirmed by Brindley and Harrison (1952) were used.

TABLE I. Analyses of chloritoid–chlorite–muscovite schists.

	1.	2.	*Niggli values.*	1.	2.
SiO_2	46·46	59·10	*si*	140·8	239·6
TiO_2	1·30	0·93	*al*	53·7	54·0
Al_2O_3	29·48	22·58	*fm*	29·9	28·7
Fe_2O_3	6·65	0·97	*c*	1·5	3·4
FeO	3·93	4·40	*alk*	14·9	13·9
MnO	0·05	0·09	*k*	0·55	0·68
MgO	1·00	1·82	*mg*	0·16	0·38
CaO	0·44	0·81	*al*−(*alk*+*c*)	37·3	36·7
Na_2O	2·24	1·12			
K_2O	4·07	3·74			
H_2O+	4·24	3·63			
H_2O-	0·09	0·16			
P_2O_5	0·09	0·17			
CO_2	n.d.	0·65			
	100·04	100·17			

1. Ritten Hamar, Unst, Shetland Islands. Analyst, N. J. Snelling.
2. Red Man, Perthumie Bay, near Stonehaven, Kincardineshire. Analysts, Avery and Anderson, Melbourne.

In most of the Stonehaven chloritoids the twin axis is [110]; this appears to be the most common twin law and has been recorded by Balk and Barth (1934) and Hietanen (1951). In one case the twin axis was [230]; this twin law has not been recorded before. Only one triclinic lamella was measured; this was intergrown with a monoclinic lamella parallel to the basal cleavage. In all cases showing monoclinic optics α was parallel to the basal cleavage, thus $\alpha = b$.

Most of the lamellae measured from the Saxa Vord chloritoids had triclinic optics, but occasional monoclinic lamellae occurred intergrown with twinned triclinic lamellae parallel to the basal cleavage. A similar intergrowth has been figured by Hietanen (1951, fig. 5). As with the Stonehaven chloritoids, $\alpha = b$ in all the monoclinic lamellae.

These determinations confirm Hietanen's observation that both

Highland Border Fault. Most of this area is now covered by forest and none of the localities could be found.

optically monoclinic and triclinic forms of chloritoid occur; but only one monoclinic form was observed, with $\alpha = b$. Previous studies have recorded monoclinic forms with $\alpha = b$ and $\beta = b$.

TABLE II. Analyses of chloritoids from Stonehaven and Unst.

	1.	2.	3.	4.	5.
SiO_2	24·36	n.d.	23·48	28·96	23·85
TiO_2	2·47	0·05	2·55	0·53	0·56
Al_2O_3	38·43	1·78	39·71	33·56	35·83
Fe_2O_3	4·13	1·09	3·79	8·43	9·00
FeO	20·14	n.d.	20·73	19·05	20·33
MnO	0·63	n.d.	0·66	0·93	0·99
MgO	1·90	n.d.	2·00	1·82	1·94
CaO	0·29	n.d.	0·31	0·32	0·34
Na_2O	n.d.	n.d.	—	n.d.	—
K_2O	n.d.	n.d.	—	n.d.	—
$H_2O+110°$ C.	6·63	n.d.	6·77	6·70	7·16
$H_2O-110°$ C.	0·03	n.d.	—	0·08	—
	99·01		100·00	100·38	100·00

Atomic proportions calculated on the basis of 14 (O+OH) *to the unit cell.*

Si		2·032	1·945	2·390	2·000
Al		3·000	3·000	3·000	3·000
Fe‴	*Y*	0·782	0·871	0·263	0·540
		0·218	0·129	0·523	0·460
Fe″	*X*	0·041	0·107		0·110
		1·405	1·435	1·314	1·425
Mg		0·236	0·247	0·224	0·242
Mn		0·045	0·046	0·065	0·070
Ti		0·155	0·159	0·033	0·035
Ca		0·026	0·028	0·028	0·031
OH		3·692	3·739	3·687	4·002
X		1·908	2·022	1·664	1·913
Y		1·000	1·000	0·786	1·000

1. Chloritoid, Saxa Vord schists, Ritten Hamar, Unst, Shetland Isles. Analyst, N. J. Snelling.

2. Partial analysis of residue after solution of Saxa Vord chloritoid in conc. H_2SO_4. Analyst, N. J. Snelling.

3. Saxa Vord chloritoid recalculated on assumption that all the alumina of col. 2 was present in muscovite and the iron in magnetite.

4. Chloritoid, Red Man, near Stonehaven, Kincardineshire. Analyst, N. J. Snelling.

5. Analysis 4 recalculated so that Si = 2; this requires the assumption that the quartz impurity amounts to 6·61%.

Chemical composition. Analyses of the two chloritoids are given in table II. Particular care was taken in the water determinations, a modified Penfield method being adopted. A silica tube was used in

place of the normal soft glass tube, and was heated with an oxy-coal-gas blowpipe. The temperature reached was sufficient to cause fusion of the samples.

An attempt has been made to correct the analysis of the Saxa Vord chloritoid for inclusions and groundmass impurities by the method used by Simpson (1931) and by Balk and Barth (1934). The mineral was dissolved in sulphuric acid, leaving a residue which consisted of inclusions, impurities, and silica resulting from the decomposition of chloritoid. It has already been mentioned that quartz inclusions are rare in the Saxa Vord chloritoid and no attempt was made to differentiate between quartz occurring as inclusions and silica resulting from the decomposition of the chloritoid. Microscopic examination of the residue revealed a high content of finely divided muscovite and iron ores; it was dissolved in sulphuric and hydrofluoric acids, and total iron, titania, and alumina determined in the usual way (table II, col. 2). Potash, silica, and water were then calculated on the assumption that all the alumina in the residue was present in muscovite; total iron was recalculated to give the proportions of ferrous and ferric iron required by magnetite, and the original analysis was corrected and recalculated to 100 % (table II, col. 3). The low summation of the original analysis is probably due to failure to determine alkalies which would occur in the muscovite impurities and possibly in the chloritoid itself.

The recent work of Brindley and Harrison (1952) has indicated that the structural formula of chloritoid may be written $(Fe^{2+},Mg)_2Al(OH)_4Al_3O_2(SiO_4)_2$. They have shown that the structure consists of layers of aluminium ions sandwiched between silicate layers in a manner similar to the occurrence of potassium ions between the silicate layers of the micas. The silicate layers of chloritoid consist of two sheets of unpolymerized SiO_4 tetrahedra the vertices of which point inwards. The divalent and hydroxyl ions, together with one-quarter of the aluminium ions, are situated within the silicate layers. The packing of the aluminium ions occurring between the silicate layers and the oxygens which form the bases of the SiO_4 tetrahedra of the layers is similar to the aluminium–oxygen packing of corundum. Since there is little replacement of Al^{3+} by other ions in corundum the present writer suggests that the small amounts of Fe^{3+}, Mn^{2+}, Ca^{2+}, and Ti^{4+} usually recorded in the analyses of chloritoid are accommodated within the silicate layers and that the general formula of chloritoid may be written: $X_2Y(OH)_4Al_3O_2(SiO_4)_2$ where X includes Fe^{2+}, Mg^{2+}, Mn^{2+}, Ti^{4+}, Ca^{2+}, and Fe^{3+} and Y includes Al^{3+} and Fe^{3+}. In view of the slight degree

of replacement of Si by Al in unpolymerized SiO_4 tetrahedra the Si values should not depart significantly from 2.

The Saxa Vord chloritoid is in good agreement with this formula even if no correction is made for inclusions. The Stonehaven chloritoid departs considerably from the suggested formula, showing a high Si content, low (OH), and low summations of the *X* and *Y* groups. However, it was impossible to separate the chloritoid from the numerous quartz inclusions and there can be no doubt that this is the cause of the high Si and other discrepancies. In table II, col. 5, the analysis has been recalculated to give 2 Si to the unit cell, the resultant formula being very close to the ideal with $(X+Y)$ very nearly 3 and (OH) a little over 4. The calculation shows that the silica of the analysis (table II, col. 4) was high by 6·61 %. These analyses are in agreement with earlier chemical studies (Milne, 1949), which showed that chloritoid was an iron-rich mineral with limited replacement of iron by magnesia.

Milne (1949) has suggested that chloritoid be grouped with the sheet silicates in which the characteristic structural element is the Si_4O_{10} sheet, and that the ideal cell content is $4(Fe^{2+},Mg)_2(Al,Fe^{3+})_2(Al_2Si_2)O_{10}(OH)_4$. As with margarite (Bragg, 1937), half the silicons in the Si_4O_{10} sheets are replaced by aluminium. The twenty analyses discussed by Milne show good agreement with this formula. Some Si values are higher than 2 but this he attributes to variations in the degree of replacement by Al. The structure proposed by Brindley and Harrison requires that Si values over 2 must be explained by the presence of quartz impurity in the analysed sample. Recalculation of the formula of the Stonehaven chloritoid in accordance with this assumption gives a result in much closer agreement with the ideal unit-cell content accepted both by Milne and by Brindley and Harrison, and provides support for the structure determined by Brindley and Harrison.

Comparison with earlier analyses and refractive index determinations shows a tendency for the refractive indices to decrease with increasing amounts of Mg replacing Fe^{2+}. There is some indication that chloritoids with high ferric iron have higher refractive indices than chloritoids with comparable FeO:MgO ratios but lower ferric iron contents.

Conclusions. Chloritoids from Unst and Stonehaven may be either monoclinic or triclinic, with $\alpha = b$ in the monoclinic varieties. Twinning is common with zone axes [110] and [230] as the twin axes; the composition face is always (001). Intergrowths of monoclinic and triclinic lamellae also occur. Refractive indices increase with increase in the FeO:MgO ratio and the Fe_2O_3 content. The formula of the Saxa Vord

chloritoid agrees well with that suggested by Brindley and Harrison. The Stonehaven chloritoid, however, has a high Si content; this is attributed to quartz inclusions, and satisfactory agreement with the suggested formula is obtained if the analysis is recalculated so that Si = 2.

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The photoelectric measurement of reflectivity.

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[Read 28 March 1957.]

Summary. A simple photoelectric-cell attachment for use with an ordinary ore-microscope is described. Stabilization of the light source and accurate calibration of the photometer enable reflectivity values to be determined within an accuracy of 1 % of the measured value. The choice of a universally acceptable standard is discussed. The photometer can be used with white light or with light of different wave-lengths. Bireflection, dispersion, and dispersion of the bireflection can readily be measured.

THE accurate determination of the reflectivity[1] of minerals in polished section has been regarded for many years as a valuable aid to their identification. Reflectivity can be measured visually or photoelectrically, but it is generally agreed that the photoelectric method is capable of greater accuracy, provided the mineral grains are not unduly small. Hitherto, however, no simple, inexpensive, and yet reliable apparatus has been described to exploit this potential accuracy fully. The photoelectric method was first employed by Orcel (1927, 1928, 1930) in France, using an alkali-metal cell. A few years later Ehrenberg and Ramdohr (1934) in Germany, and Moses (1936) in the United States of America, independently conducted detailed investigations on the reflecting power of minerals using rectifying cells. More recently Folinsbee (1949) has made a contribution to the simplification of reflectivity measurements by employing a standard photographic exposure meter coupled directly to an ore-microscope; but the accuracy sacrificed by the employment of this technique more than outweighs its advantages. A further drawback of Folinsbee's method from the point of view of practical mineragraphy is that measurements cannot be made on grains less than 1 mm. across.

The apparatus described in this paper has been used for six years and during this time has proved to be not only robust and reliable but capable of measuring the relative reflectivity of ore minerals within the desired precision of plus or minus 1 % of the measured value. The photoelectric-cell characteristics have been tested periodically through-

[1] Defined as the percentage of normally incident light reflected from the surface

out the trial interval, and, as they have not changed appreciably, the apparatus seems to be highly satisfactory in every way. Measurements can be made on grains of about 0·06 mm. in diameter using a 4-mm. objective, and 0·04 mm. with a 1·8-mm. oil-immersion objective. The accuracy of the measurements made on grains of these minimum sizes is not always within the accuracy quoted above, but simple modifications to the apparatus described, such as using a more sensitive galvanometer and a more powerful light source, could enable measurements of the required precision to be made. This, however, is not considered necessary for general use.

Description of the apparatus.

The essential components of the apparatus are an ore-microscope with a tube iris diaphragm, a selenium barrier-layer cell in a suitable holder, and a sensitive galvanometer with a relatively low internal resistance. In localities where there are large fluctuations in both mains voltage and frequency, the light source must be stabilized, but elsewhere this refinement is not essential for diagnostic purposes.

Microscope. A microscope with a cover-glass reflector unit, bloomed objectives, and external illumination is necessary for good results. That used by the writer is a standard Cooke, Troughton, and Simms ore-microscope to which an additional iris has been fitted in the tube just below the base of the ocular. The purpose of this iris is to cut out stray light reflected from minerals outside the field being examined. Use could be made of the iris diaphragm normally available on microscopes fitted with a Wright slotted ocular, and the cell could be mounted in the accessories carrier. Whatever type of housing is used for the cell it is essential for accurate work that an iris be provided as near as possible to the sensitive surface of the cell.

Cell holder. The cell holder was designed so that it could replace the ocular easily and in such a way that the sensitive surface of the cell would always take up a position in the plane of the primary image of the mineral under examination.

The construction of the cell mount shown in fig. 1 is probably more elaborate than necessary, but as this is essentially an experimental model it was necessary to make it so that the cell could be replaced easily and filters introduced below the sensitive surface.

Galvanometer. A spot galvanometer is employed with an internal resistance of 450 ohms and with a linear scale graduated from 0 to 100; it is manufactured by the Cambridge Instrument Company Limited.

Photoelectric cell. Photoelectric cells of barrier-layer type offer several advantages over gas-filled or vacuum cells for measurements of the type described here. The most important of these are long life, robustness, compactness, and the ability to deliver an electric current without the necessity of applying an external potential. The current generated

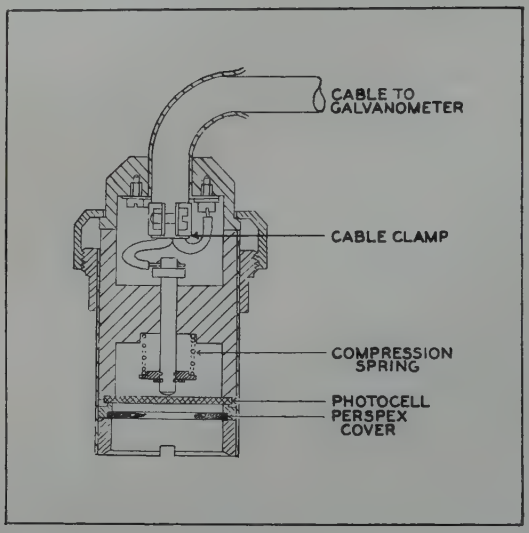

FIG. 1. Section showing construction of the cell mount.

when the sensitive surface of the cell is illuminated is directly proportional to the illumination when, as in this case, the internal resistance of the cell is high and the external load resistance is comparatively low.

Of the cells tested, the selenium barrier-layer type manufactured by Evans Electroselenium Limited delivered the greatest current for a given intensity of illumination, gave near linear response over the range of illumination used, and showed no signs of fatigue. One 'EEL' cell has been in operation for over six years and no appreciable change in its characteristics has yet been noted.

Stabilization of the light source.

One of the major problems in the use of photoelectric techniques for measuring reflectivity under an ore-microscope is the stabilization of the light source. A number of methods have been tested, including the use of a constant-voltage transformer and the use of high-capacity accumulators alone, but only one of the methods tried has produced satisfactory results. Typical readings, taken at the same time of day in

each case, are given in table I to show the effect of using unstabilized light, light stabilized by a constant-voltage transformer, and light stabilized by the method finally adopted.

TABLE I. The effect of various lighting circuits on the observed reflectivity. A pyrite standard was used and the irises adjusted to give an initial reading of 54·5 in each case.

Time.	Unstabilized illumination.	With constant-voltage transformer.	Stabilized illumination.
1500 hours	54·5	54·5	54·5
1505 „	53·5	54·0	54·5
1510 „	54·0	54·6	54·5
1515 „	54·6	54·0	54·4
1520 „	54·2	53·9	54·5
1525 „	53·9	53·9	54·5
1530 „	54·0	54·0	54·5

The arrangement employed is shown diagrammatically in fig. 2. A constant-voltage transformer (TR), which has coarse (C) and fine (F) adjustment controls on the output current, is used to supply a partially stabilized current to a heavy-duty accumulator charger (CH). The battery (B), which is kept charged, has the requisite number of heavy-duty car-starter cells and is connected in series with a −10, 0, +10

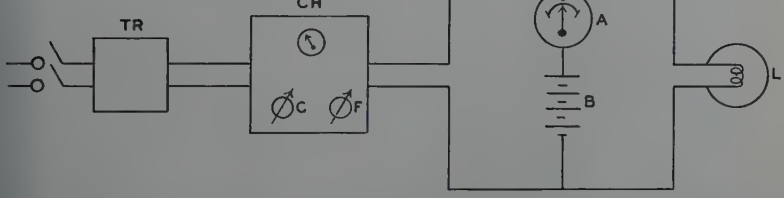

FIG. 2. Diagrammatic layout of the stabilization circuit. TR, transformer; CH, charger; C, coarse adjustment; F, fine adjustment; A, ammeter; B, battery; S, switch; L, lamp.

ammeter (A) across the charger. The lamp (L) used by the writer is a compact tungsten filament type that consumes 48 watts at 8 volts and hence requires a current of 6 amps. This is supplied by the charger, which is normally adjusted by the fine control to give an ammeter reading of zero.

The stabilizing effect of the heavy-duty battery in this circuit results from its very low internal resistance. Any fall in the current supplied through the charger would be compensated for by current taken from

the battery; and any excess current from the charger would be diverted through the battery.

It is necessary to give the battery a charge periodically. This can be achieved simply by opening the lamp switch (s) while the charger is still operating. After charging, the battery voltage should be allowed to settle for an hour or so before it is used again for making accurate measurements. During normal use the battery and light are switched off simultaneously.

Calibration.

One of the main disadvantages of the early barrier-layer cells was the variability in sensitivity over their surface. Obviously this would have been a serious drawback to accurate measurements, and one of the first tasks of calibration was to test the response of the cell over its entire surface. To do this a disc from which a one-eighth sector had been machined out was placed beneath the cell in the holder and rotated through a complete circle; at the same time the light falling on the cell was kept constant. No variation in galvanometer reading was observed during the rotation of the disc through 360°.

The next step in the calibration of the instrument was to determine whether the response of the combined cell and galvanometer was linear. This was done in two ways. Firstly, a highly reflecting mineral was placed on the microscope stage and the field iris opened until the reading on the galvanometer was 100. Discs from which $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ sectors had been cut were then inserted in turn in the cell holder and the readings noted. The results shown in fig. 3 demonstrate that the response is linear. A second test, which checked not only the linearity of the response but also its reproducibility, was made by inserting accurately calibrated neutral density filters in front of the light source. The results of this experiment are shown in table II. The filters were calibrated by the National Physical Laboratory using a tungsten filament lamp operating at a colour temperature of 3050° K., which is the same as that of the microscope lamp employed. The percentage transmission values measured photoelectrically agree closely with those determined by the National Physical Laboratory. However, as there is some variation from cell to cell, new cells should always be tested for linearity before use.

Choice of reflectivity standard.

The choice of a reflectivity standard has been the subject of discussion for many years, but none has yet been universally accepted. This is

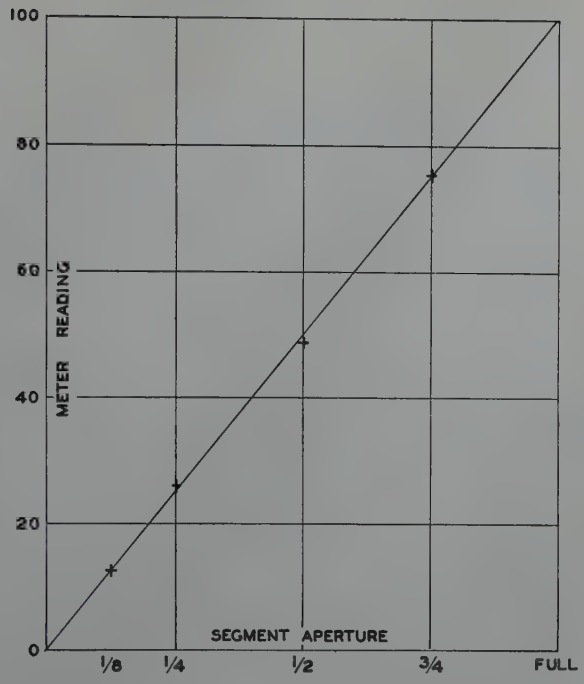

FIG. 3. Graph demonstrating the linear response of the photoelectric cell and galvanometer.

TABLE II. Calibration data on three EEL cells.

Density*.	Percentage transmission.	EEL cell No. 551.	EEL cell No. 1054(*a*).	EEL cell No. 1054(*b*).
0·114	76·9	77·0	77·0	77·5
0·310	49·0	49·0	49·0	49·1
0·542	28·7	28·7	28·5	28·2
1·046	9·0	9·0	9·0	8·9
2·159	0·7	0·7	0·7	0·7

* Defined as the logarithm of the reciprocal of the transmission of the neutral filter used.

partly owing to the difficulty of making absolute reflectivity measurements at normal incidence and partly to the lack of an ideal substance. A good standard should have a high reflectivity with little dispersion and should be isotropic; it must be free from inclusions and flaws, should polish easily without being scratched, and should have a high resistance to tarnish.

Theoretically, the reflectivity (R) of a transparent isotropic medium at normal incidence in air can be calculated from the Fresnel equation:

$$R = \frac{(n-1)^2}{(n+1)^2} \times 100,$$

where n is the refractive index. A highly refracting mineral like diamond can therefore be used as a primary standard, the reflectivity being calculated for light of different wave-lengths from the corresponding refractive indices. Even diamond, however, has too low a reflectivity (17·2 in sodium light) for it to be an ideal standard, and complete elimination of internal reflections is a difficult matter. As will be shown below, a carefully cut diamond may be used as a primary standard with which to establish the best reflectivity value for a secondary standard for routine use. Blende has sometimes been used as a standard, but compared to diamond it has the additional disadvantage that its reflectivity depends on its iron content.

Several pure metals, namely copper, silver, rhodium, and platinum, have been examined for use as secondary standards, but none proved entirely satisfactory. A large number of mineral species have also been considered and eventually pyrite was chosen as the most suitable. Its surface does not tarnish readily and its reflectivity, which is remarkably constant from specimen to specimen, lies near the middle of the range found in ore minerals. Sections of pyrite from ten different localities give values in white light within 0·1 of each other. This, of course, does not necessarily mean that all pyrite will have the same reflectivity, and as a precaution against this eventuality material from Rio Marina, Elba, is specified as being suitable. The only demerit of pyrite is that it has a rather high dispersion over the visible light range. However, the dispersion curve is relatively flat over the region from red to green normally used in dispersion measurements.

The reflectivity of pyrite for light of different wave-lengths was measured using a primary standard of diamond, specially cut to eliminate internal reflections. The values calculated for diamond (for the mean wave-lengths of the transmission bands of the filters used) are given below, together with the corresponding values determined for pyrite:

	Wratten 58. Green.	Wratten 22. Orange.	Wratten 25. Red.
Diamond	17·1	17·2	17·3
Pyrite	52·8	54·5	54·3

The reflectivity of pyrite for a tungsten filament light source operating at a colour temperature of 3050° K. was estimated to be 52·8 by the same method, assigning a value of 17·2 to diamond. Since, however, values are available (Folinsbee, 1949; Uytenbogaardt, 1951) for the reflectivities of some 200 mineral species measured relative to pyrite at 54·5, the latter value has been adopted as an interim measure until sufficient new and more accurate data are available. The values quoted above are regarded as tentative and are subject to revision in a future communication.

Use of the photometer.

Measurement of reflectivity. To obtain the reflectivity of an unknown mineral the pyrite standard is first placed on the stage, brought into focus, and a scratch-free area selected. The ocular is then replaced by the cell unit and the field and tube irises adjusted till a reading of 54·5 is obtained on the spot galvanometer. A box with a circular hole in the top and painted dead black inside is then placed immediately under the objective and the sub-stage raised until the bottom lens of the objective fits just inside the hole. A second reading is taken on the galvanometer and the zero-setting control adjusted until it reads zero. (This reading is necessary to compensate for stray light reflected mainly from the top surfaces of the lenses in the objective.) The standard is then replaced and the irises adjusted slightly to restore the reading of 54·5. Next, the unknown is placed on the stage, focused carefully, and a suitable area chosen as before. The new reading obtained when the cell has been put in position is then given directly on the galvanometer as percentage reflectivity. Once the microscope has been set up in this way, it is not necessary to take any further measurements with the standard unless the area of field controlled by the irises is changed. If great accuracy is required, readings for the standard should be obtained immediately before and after the unknown.

For best results specimens must be well polished. The criterion of a good polish is that the surface should be flat and without visible scratches at the magnification employed. The surface should be cleaned with benzene and a lens tissue before the measurement is made. (Buffing on a chamois leather pad tends to scratch soft minerals, though it is suitable for hard ones.) There is little evidence that the method of polishing has any effect on reflectivity values, but this is being investigated more fully. Tests carried out on five minerals polished with aluminium oxide and with magnesium oxide on lead laps and with

aluminium oxide on a cloth lap showed no appreciable difference in reflectivity provided the specimens were equally well polished by the three methods. Results of this experiment are given in table III:

TABLE III. Reflectivity values obtained after different polishing techniques.

	Al_2O_3	MgO	Al_2O_3
Mineral species.	Lead lap.	Lead lap.	Cloth lap.
Pyrite	54·5	54·5	54·5
Davidite	17·2	17·2	17·2
Uraninite	16·8	16·9	16·8
Blende	17·5	—	17·4
Tetrahedrite	30·7	30·7	30·8

Bireflection. The polished surfaces of isotropic minerals give one reflectivity value in the same way as such minerals have one refractive index in transmitted light. Similarly, most sections of anisotropic minerals have two principal directions which differ in their reflecting power for rays vibrating along them. It is a simple matter to measure the maximum and minimum reflectivity in any section by rotating the stage until these values are observed. The difference between the two values gives a measure of the bireflection of the section. Any particular section may not exhibit the maximum bireflection of the mineral, just as in any thin section the maximum birefringence may not be observed; but if a number of grains of the same mineral are examined (and this can be done very quickly) the maximum and minimum values can usually be determined without much effort. Where crystallographic directions can be observed, it is always useful to note the relationship between these and the principal directions. The numerical value of the bireflection is a valuable aid in mineral identification.

Dispersion. The reflectivity of most minerals varies with the wavelength of the incident light and unless its spectral composition is defined there is little point in employing precise photometric methods for measuring the reflectivity. Unfortunately the use of a monochromator or of filters that transmit a narrow spectral band cuts down the intensity of the illumination so drastically that either a very powerful light source must be employed or the output from the electric cell must be amplified. The first alternative introduces stabilization difficulties, as the heavier the current required the less easy it is to obtain satisfactory stabilization of the light source. The second alternative makes the whole apparatus rather complicated for general use.

It is recommended that for normal diagnostic purposes a compac

tungsten filament lamp operating at a colour temperature of 3050° K. be employed and that the Wratten filters be used to give a measure of dispersion of the reflectivity. It is usually sufficient to note whether the reflectivity increases or decreases with increase in the wave-length of the incident light.

TABLE IV. Selected minerals arranged in order of increasing reflectivity. The values are for measurements in air relative to a pyrite standard of 54·5.

Mineral species.	Reflectivity in white light (3050° K.)		Reflectivity in orange light (Wratten 22 filter).		Folinsbee's 'best values'.
	Range.	Mean.	Range.	Mean.	
Cassiterite	11·2–12·8	12·0	11·0–12·5	11·7	12·9
Covelline	7·0–22·0	14·5	5·0–20·0	12·5	9·5–15·1
Goethite	16·1–18·5	17·3	14·8–17·0	15·9	16·1
Blende	—	17·5	—	16·9	17·8
Ilmenite	17·8–21·1	19·4	17·3–20·2	18·7	19·4
Magnetite	—	21·1	—	20·9	21·1
Alabandite	—	23·4	—	22·0	23·9
Cuprite	—	27·1	—	24·3	27·7
Hematite	25·0–30·0	27·5	24·0–27·2	25·6	27·2
Tetrahedrite	—	30·7	—	29·4	31·2
Bournonite	36·0–38·2	37·1	34·0–35·0	34·5	35·5
Pyrrhotine	38·0–45·2	41·6	39·7–44·5	42·1	39·9
Galena	—	43·2	—	41·7	42·4
Chalcopyrite	42·0–46·1	44·0	41·0–44·8	42·9	43·2
Linnæite	—	49·5	—	49·2	47·4
Arsenopyrite	51·7–55·7	53·7	51·3–54·0	52·6	52·4
Niccolite	52·0–58·3	55·1	54·0–61·0	57·5	52·6
Altaite	—	65·5	—	62·2	63·2
Gold	—	74·0	—	80·6	73·4
Antimony	72·0–77·1	74·5	70·5–74·1	72·3	74·4

Dispersion of bireflection. The reflectivities corresponding to the two principal directions in the surface of an anisotropic mineral often vary independently with the wave-length of the light employed. This property is termed 'dispersion of the bireflection'; it can readily be measured with the apparatus described here, and may in some instances be of considerable diagnostic value.

Results. Table IV lists some typical measurements for white light and for orange light (Wratten 22 filter). They are compared with values given by Folinsbee (1949) for white light to illustrate the measure of agreement obtained with two quite dissimilar electric cell photometers. The ranges given for anisotropic minerals were measured on randomly oriented sections and indicate the degree of bireflection, though the

extremes recorded are not necessarily maximum and minimum values for the species.

Conclusions.

Provided precautions are taken in calibration, apparatus of the type described can be relied on to measure the reflectivity of ore minerals relative to a standard with a precision of better than 1 %. Reflectivities of 50 and over can normally be measured to a precision of $\pm 0{\cdot}2$. This degree of precision is much better than can be obtained by visual methods, which are limited by the inability of most observers to detect a difference of less than about 2 % in the intensity of two adjacent areas (Hallimond, 1953). The apparatus is inexpensive, can be used with any ore microscope, does not suffer from fatigue, and can be operated with little manipulative skill.

When the apparatus is used in conjunction with a micro-indentation hardness tester fitted to the same microscope (Bowie and Taylor, 1957), the two constants thus determinable with a high degree of precision enable ore minerals for which the necessary data are available to be identified in much less time than has hitherto been possible.

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Direct measurement of standard reflectances with the microphotometer.

By A. F. Hallimond, M.A., Sc.D.

[Read 28 March 1957.]

Summary. A visual microphotometer depending on three polarizing screens is used to provide the primary scale for measuring the ratio of intensity between the incident and reflected beams for a prepared standard surface, which is intended for subsequent use in the ordinary procedure with the ore-microscope. A reversing mirror on the microscope stage gives reflection at quasi-normal incidence. Direct measurements on a surface of diamond confirm the validity of the Fresnel formula for a polished surface of this substance, and there is general agreement for a series of transparent bodies ranging up to 17 % reflectance. The standard is a glass-covered metallic surface with a reflectance near 50 %. For pyrite $R_D = 54{\cdot}5$ %.

REFLECTANCE for small and irregular grains under the microscope is conveniently measured visually by the microphotometer; the measurement being made by comparison with a standard surface of known reflectance. The standard itself should as far as possible be immune from tarnish or other changes, and its reflectance at normal incidence must be ascertained by an experimental determination in which the intensities of incident and reflected light are directly compared by means of a photometer operating according to a known intensity law (Walsh, p. 190).[1] At present the basic determination can be carried out on one of three adequate types of photometer: the inverse square apparatus so widely used in optical bench methods, the calibrated photo-cell, and the polarization photometer in its recent accurate form with three polarizing filters. The latter is here employed.

Photometer. A Cooke, Troughton, and Simms visual microphotometer, of the type designed by the present writer (1953, p. 131), replaces the usual eyepiece in an ore-microscope of which the stage can be lowered to accommodate a special apparatus with reversing mirror. This photometer has two fixed parallel discs of polaroid with high polarizing ratio, between which a third disc with a graduated circle rotates giving an intensity closely in accordance with the law $I \propto \sin^4\theta$ (W. H. Steel, 1951). For the comparison, which is visual, the Lummer-Brodhun cube is abandoned in favour of a small inclined metallized reflecting surface. Comparison depends upon the matching of this area with the adjoining

[1] For full discussion of this and similar details references have been given to the textbook Photometry by J. W. T. Walsh (2nd edn, 1953).

microscope field, and does not rely upon the disappearance of the boundary, a method liable to inaccuracy (Walsh, p. 202). The photometer lamp transformer was supplied in parallel with the second lamp from a common voltage regulator (230 volts) and the lighting was adjusted so that the middle range of the divided circle (70° to 35°) was in use. All readings were taken on the same side of the zero, but a zero correction (0·6°) was separately determined and applied throughout.

Monochromatism. All readings were made in monochromatic light obtained by supporting a colour screen over the eyepiece. The screens were Ilford 'spectrum' gelatine filters, having effective band widths not exceeding 250 Å. This is the widest band suitable for accurate measurements on the dispersion of reflectance in most metals and minerals since the standard here prepared has nearly linear dispersion this band width will not be a source of error in its determination.

Matching is easiest for a yellow colour, and for this and other obvious reasons the use of the yellow (sodium) screen might well be given priority in general determinative work. When the field intensity is too low to permit the easy focusing of scratches, &c., the facility of matching diminishes, but the average value is still useful. Too bright a field causes retinal fatigue.

Lamp. The lamp was an ordinary 150-watt bulb in a cylindrical lamp house with a single condensing lens and ground glass. It provided an illuminated disc $3\frac{1}{4}$ inches in diameter (surrounded by a black screen) and was supported at a distance of about 2 feet from, and in line with the inclined spindle of the reversible mirror. Thus the beam was incident on the mirror at the same angle in the direct and reversed positions. This lamp was supplied from the same voltage regulator as the photometer. With the 33-mm. objective this diameter and distance provided an aperture cone about equal to that of the photometer.

Reversing mirror for measurement at quasi-normal incidence.

If a mirror is inclined so as to reflect a uniform beam coming from a distant lamp at right angles to the line of sight, its surface will appear to be uniformly illuminated, an effect known as the 'Maxwell view' (Walsh, p. 152). If it is then turned through 180° about an axis in the direction of the lamp, the light from it can be reflected back upon the surface under test and an image of the mirror will be formed within the surface.

When the inclination of the mirror to the rotation axis is exactly 45° the edge of the mirror will overlap and obscure the image reflected from

the test surface at normal incidence; but by altering this angle by a few degrees a sufficient area of the reflected image can be made visible beyond the edge of the mirror. The intensities of the direct image and of that reflected in the surface can then be measured with the photometer, their ratio being the reflectance for quasi-normal incidence.

The mirror is a small polished surface of stainless steel inclined at $48\frac{1}{2}°$ to the spindle. It is useful to leave a few coarse scratches or particles

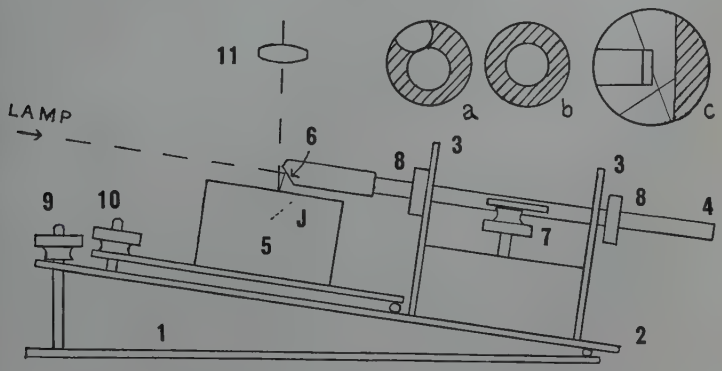

FIG. 1. Inclined reversing mirror for measuring reflectance.

on the surface both for focusing the surface and to identify the same area when the mirror is reversed (fig. 1*c*).

The arrangement for use on the microscope stage is shown in fig. 1. The base plate 1 can be fixed to the stage by two screws as usual so that the rotation axis intersects the axis of the microscope. The rest of the instrument is supported on the plate 2 which is inclined at 7°. This is equal to the angle of incidence for the axial ray of the beam that will be used. Two bearings 3 support the spindle 4 which is parallel with 2. The surface to be tested is set up in a mount 5; it stands on the inclined plate and is parallel with the spindle. At the end of the spindle is the mirror 6. By means of two adjustable stops 7 the rotation of the spindle and mirror can be arrested at two positions separated by 180°. The spindle is free to move for about $\frac{1}{8}$ inch axially so as to allow the image of the desired area to be brought under the comparison area of the photometer in the field of the microscope. Since this movement is often repeated it is convenient to have adjustable stops 8 on the spindle.

Adjustment. The mirror is directed upward with the spindle advanced toward the lamp. A suitable area is selected and focused (fig. 1*c*). When the mirror is reversed and withdrawn as in fig. 1 the same area must be

seen under the photometer when the microscope objective 11 has been lowered so as to bring the reflected image J into focus. At the same time the aperture relations of the beam are checked by inspecting the Ramsden circle with a Becke lens. The required geometric conditions should be sufficiently realized in the construction of the apparatus, so that the image of the lamp is already visible at the back of the objective (fig. 1*a*) in both the direct and reversed settings of the mirror, but it is convenient to provide two adjustment heads 9 and 10 for small final adjustments of this image in the direction of the spindle, while the stops 7 control the position at right angles. Heads 10 and 7 also serve to correct the levelling of the mount. These adjustments must not involve a departure of more than, say, one degree from the strict geometric conditions. By this means the image of the lamp is adjusted to coincide with the aperture disc of the photometer, for both the direct and the reversed settings of the mirror (fig. 1*b*). The disc occupies about one-half of the diameter of the 33-mm. objective (N.A. 0·1) and represents an incident cone of about $\pm 3°$ surrounding the axial ray, which is incident on the object at 7°. Careful checking is essential, otherwise errors may arise from the Stiles–Crawford effect (Walsh, p. 59); for the present photometer the artificial pupil is about $1\frac{1}{2}$ mm. in diameter. Readings are then taken for the intensity of the focused image of the mirror, alternately in the direct and reversed settings. For the present purpose ten pairs of readings were averaged for each determination. There is no correction for reflection in the objective; the value of R is simply the ratio of the two intensities obtained from the table of $\sin^4\theta$ (Manual, p. 194).

A standard reflecting surface.

A standard for general use is best chosen with a reflectance of about 50%. Cleavage planes cannot be relied on to provide a sufficient area; it was therefore made from a polished metal. An open metal surface requires to be repolished at intervals, and this leads to some uncertainty due to different methods of preparation. The covered standard here used was prepared by Mr. B. O. Payne; it consists of a surface plated with the alloy 'inconel', polished and covered with a thin coverglass cemented with balsam. Although in the end some change is to be expected, this standard remains constant over a considerable period and only requires to be cleaned like a glass lens before use. It can be redetermined when required. The thin glass is uniform in effect and does not interfere with the use of the standard at low magnification. Average values were, for mean wave-lengths in mμ: λ 670, 54·6;

λ 650, 54·1; λ 580, 51·8; λ 520, 49·0; λ 490, 47·3 %. Duplicates can be checked by the photocell.

Verification of the Fresnel formula for transparent mineral standards.

Transparent minerals are subject to errors from back reflections; these can be eliminated by using a shallow prism, such as a 12° prism of sapphire (A. F. Hallimond, 1956, p. 135). Diamond seems an ideally suitable material, though its reflectance (17·2) is still rather low for general use.

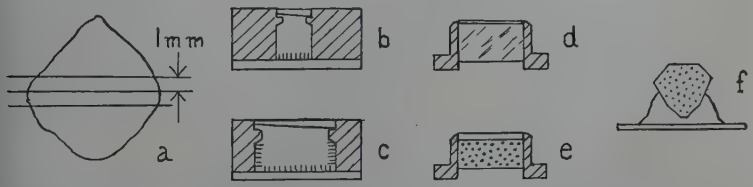

FIG. 2. Photometric standard surfaces. *a*, method of cutting the diamond octahedron; *b*, diamond prism mounted in ebonite with a black velvet surface underneath; *c*, sapphire prism over a box lined with black velvet; *d*, surface plated with 'inconel' metal under a coverglass; *e*, basal section of quartz mounted on clear 'black' glass; *f*, a cut garnet.

The prism (see below) has an angle of 5°. This value was chosen as the minimum that would throw the back reflection clear of the objective, while using the least possible thickness of diamond. It was mounted with the top surface level, over a small cavity lined with black velvet (fig. 2*b*). It is not necessary to varnish the back of these prisms.

The Fresnel formula. Although the reflectance can be calculated by the formula $(n-1)^2/(n+1)^2$, it is not *a priori* certain that the surface as prepared will give exactly this value. Direct measurements were accordingly made by the present method, on diamond, garnet, and sapphire. The direct beam is here so much brighter than the reflected that it was found useful to lay a neutral glass screen (transmitting about $\frac{1}{5}$) over the eyepiece while the direct measurement was made. Any change in the Fechner ratio is more than compensated by the avoidance of the bright alternate readings, which cause retinal fatigue.

Reflectance for Ilford screen 606, wave-length 580 mμ.

Mineral	Observed values (each 10/10 pairs)					Mean	Calc.	Refr. ind.
Diamond	17·3	17·6	17·4	17·6	17·2	17·4	17·23	2·419
Sapphire	7·6	7·7	—	—	—	7·6	7·7	1·77
Garnet	8·2	8·2	—	—	—	8·2	8·3	1·809

The sapphire and garnet were polished for one or two minutes with $\frac{1}{4}$ μ diamond paste on selvyt, and cleaned with CCl_4. In garnet the interna reflection is absorbed by the strongly coloured mineral.

Minor errors. The distance between the lamp and the objective is the same in the direct and reversed settings apart from the small increase due to the axial withdrawal of the mirror by $\frac{1}{8}$ inch. In 24 inches this causes a change in intensity equal to 1 per cent., the observed value of I being too low by that amount. The loss is, however, compensated by the fact that the stainless steel mirror caused a weak polarization, the component perpendicular to the plane of incidence being brighter in the ratio (measured) 6:4. Although the mean value of the two component after quasi-normal reflection in the object should still be very close to the true normal value for R, the predominance of the higher componen will cause a slight increase in the observed value.

After allowing for these details, the above results seem sufficiently in agreement with the Fresnel formula to justify the calculated values fo the three minerals. With quartz (fig. 2*e*, $R = 4{\cdot}58$) they form a useful series when surfaces of lower reflectance are required.

Reflectance of Pyrite.

Pyrite has sometimes been used as a standard, the reflectance deter mined by Orcel being 54 % at λ 590 mμ. Since the screens commonly used transmit rather wide bands, it may be of interest to record a series of direct measurements by the present method with 'spectrum' screens.

An irregular crystal of pyrite from Rio Marina, Elba, containing plates of hematite, was polished as usual. Before each set of readings the surface was polished for 1 minute with γ-alumina in 'DC 703' silicone on selvyt, and cleaned with CCl_4. After one or two days the reflectance of pyrite diminishes, but there seemed little difference in the present results taken within a few hours of polishing.

Each value is the mean of ten pairs of readings, reflected/direct, and is represented by a circular point in fig. 3. As an independent test, the reflectance was also measured in the ordinary way, by substitution with the standard 'inconel' surface prepared above; these results are shown as open circles. For each indirect value six settings were averaged for pyrite, then for the inconel standard. The results, which may be regarded as typical of those to be expected in ordinary determinations, seem in sufficient agreement with the direct series, thus confirming the use of this standard.

The mean values in the direct series for pyrite are:

λ	470	490	520	550	580	610	650	670	mμ.
R	49·1	50·9	52·6	52·7	54·3	55·1	56·4	55·0	%

The reflectance falls off rather steeply towards the blue (Orcel records 43 at 460 mμ). There is a maximum in the red followed by a small

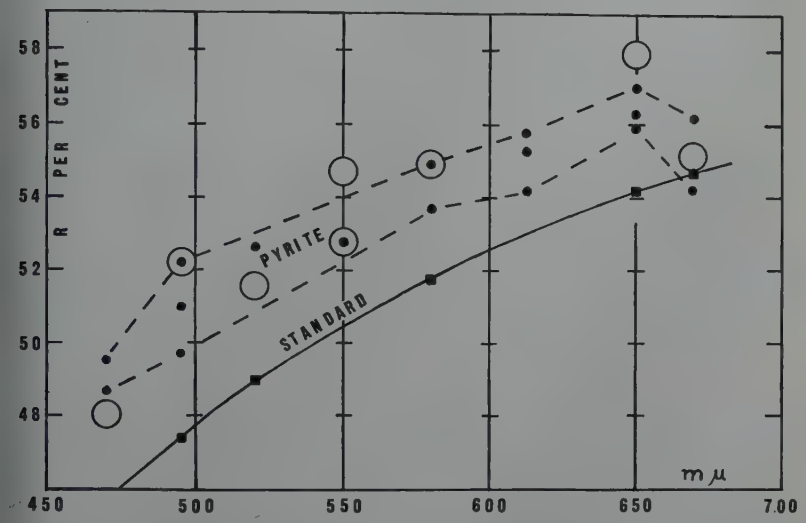

FIG. 3. Dispersion of reflectance. Values for 'inconel' standard (■), and for pyrite (direct, ●; by comparison with 'inconel' standard, ○).

reduction at the last, deep red, wave-length. This seems to agree with the values recorded for a 'red' screen (Ramdohr, 1950, p. 572) though at a somewhat longer wave-length.

In sodium light the value $54\frac{1}{2} \pm \frac{1}{2}$ is indicated for pyrite.

Preparation of the standard diamond prism.

The late Dr. P. Grodzinsky (Industrial Distributors Ltd., Diamond Research Department, Holborn), who very kindly provided the diamond prism here used, supplied the following details of the preparation of four prisms.

The raw material was two octahedral diamonds each of about 0·6 carat. These diamonds were sawn by Mr. Lever, Woodbridge House, in the way indicated in fig. 2*a*; i.e. the diamond was sawn through the girdle, and two additional saw cuts were made, one on each of the remaining

half pyramids. The thickness of the plate was about 1 mm. Subsequently the side faces were finely polished and the angle of 5° taken off one side by Messrs. A. and P. Rotenberg. The result was a plate approximately $4\frac{1}{2}$ mm. square. This emits very little diffuse light when under the full intensity of the ore-microscope. There are still some variations in level, but these do not affect the readings since they will only cause a slight spreading of the aperture disc. The surface finish of diamonds has recently been investigated by A. L. Bailey and M. Seal (1956) and by E. M. Wilks (1953). Polish scratches are everywhere present; they may average 0·01 mm. apart and up to 1,000 Å. in depth, but the depth is reduced by finer polishing. In the present case the aperture disc is well defined and there seems no appreciable loss of light by diffusion at the surface, the reflection being essentially specular.

Acknowledgements. The author is indebted to Mr. B. W. Anderson for kindly providing the prism of synthetic sapphire and for the loan of specimens, to the late Dr. P. Grodzinski for the diamond prism described above, and to Mr. B. O. Payne of Messrs. Cooke, Troughton, and Simms, Ltd., for the preparation of experimental standard surfaces, including that described.

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SHORT COMMUNICATIONS

An occurrence of axinite in Ventersdorp lavas from Kinross, Transvaal, South Africa.

Axinite-bearing veins were found in diamond-drill cores of Ventersdorp andesitic lavas from the Kinross area, which lies approximately seventy miles east of Johannesburg. Apart from an occurrence in the greenstones of Southern Rhodesia,[1] there is no published record of axinite from elsewhere in southern Africa. The lavas are dark green and fine-grained, diabasic in texture and occasionally amygdaloidal. Thin section shows laths of plagioclase with subangular leucoxene in a fine-grained chloritic ground-mass. Amygdales contain chlorite, quartz, and calcite. In the immediate vicinity of veins the lava has been altered, bleached, and epidotized, with magnetite granules concentrated towards the vein margins.

The central parts of the veins consist of axinite with the main cleavage trace apparently perpendicular to the marginal quartz mosaic. Thin late quartz veinlets in the axinite are often cut by stringers of calcite, which is also frequently seen as small euhedral crystals. There are fine radiating needles of actinolite in the axinite, and small grains of chalcopyrite and pyrrhotine are sparsely scattered throughout the veins. Axinite was also observed in a quartz–orthoclase vein, which carries columnar epidote, clinozoisite, and a little prehnite in typical 'bow-tie' structure. The occurrence resembles that in a diabase described by Steinwachs.[2]

The axinite was cleaned for physical measurements and chemical analysis by careful hand-picking of coarsely-crushed material. After further crushing the sample was freed of impurities by electro-magnetic treatment, heavy liquid separation, and acid washing. An analysis by C. E. G. Schutte, of the Division of Chemical Services, Pretoria, gave I; for comparison, two recent analyses of axinite from Kongsberg, Norway,[3] and the sub-polar Urals[4] are given (II and III):

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.	Na_2O.
I.	45·80	17·29	2·34	6·03	0·93	2·19	18·62	0·22
II.	42·40	18·22	0·53	5·83	4·42	0·83	19·72	0·14
III.	42·60	17·04	·0·47	7·56	3·52	1·84	19·28	0·42

	K_2O.	B_2O_3.	TiO_2.	P_2O_5.	H_2O+.	H_2O-.	Sum.	Sp. gr.
I.	0·20	3·85	0·20	0·26	1·65	0·05	99·63	3·23
II.	0·03	6·05	—	—	1·60	—	99·77	3·299
III.	—	5·43	0·08	—	1·04	0·36	99·64	3·33 to 3·35

The formula calculated on the basis of 17 (O,OH) atoms suggests an excess of silica, probably as extremely fine quartz veinlets in the axinite.

Refractive indices for sodium light were determined as α 1·677, β 1·684, γ 1·687 (all $\pm$0·002). Similar values were obtained for red and green light. The axial angle was measured on the universal stage; except for one direct measurement, all the crystals investigated showed one axis only. The average of readings by four observers gave for different wave-lengths: $2V_\alpha$ 73·0° (650 mμ), 73·5° (580 mμ), 72·5° (520 mμ), 72·5° (470 mμ), and 72·0° (daylight). These results do not really indicate any dispersion. $2V_\alpha$ calculated from the refractive indices is 74·5°. Comparison of the values of the optic angle with the chemical composition of various axinites suggests that there is no relationship between composition and optic angle. A slight pleochroism was observed in thicker sections and varied from lilac-pink to yellow-pink; but no pleochroism could be detected in sections of standard thickness. No fluorescence was observed in ultra-violet light of various wave-lengths.

In conclusion it is suggested that the pneumatolytic stage of the Bushveld granite may have contributed to the formation of axinite-bearing veins at Kinross.

Acknowledgements. It is with pleasure that we thank Messrs. A. Frost and E. F. Marland for providing the facilities for examining the cores. We thank the Director of the Union Geological Survey for the chemical analysis. We are indebted to Dr. J. J. Frankel, under whose guidance this research was carried out, for his interest and encouragement. The Union Corporation, Ltd., has given permission for the publication of this paper.

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Cryptomelane from Mysore (India).

While examining under the microscope a polished section of a specimen of manganese ore from the Kumsi area (My 15, Gange-Gowri Workings, Kumsi area, Shimoga District), I came across a very fine-grained greyish-white mineral associated with psilomelane, showing a slightly lower hardness[1] than psilomelane. Etch tests were not conclusive because of the fine-grained nature of the mineral and its intimate association with psilomelane and pyrolusite; to obtain conclusive results the X-ray powder method was used. With the help of a micro-drill, a little powder of the mineral was removed from the polished section and an X-ray photograph taken by the Debye-Sherrer method using Fe-$K\alpha$ radiation without filter.

The d spacings observed from the film, tabulated below, agree fairly well with those given by Mathieson and Wadsley (1950) for a cryptomelane from the Chindvara district.

d Å.	I.	d Å.	I.	d Å.	I.
7·03	40	2·40	100	1·38	10
4·97	30	1·83	50	1·35	20
4·32	20	1·65	60	1·19	10
3·36	40	1·54	20	1·17	10
3·14	70	1·42	10	1·15	20
2·45	10	1·39	10	1·07	20

According to Anders and Marie Byström (1950), cryptomelane, hollandite, and coronadite form an isostructural series of the general formula $A_{2-y}B_{8-z}X_{16}$, where $A = Ba^{2+}$, Pb^{2+}, K^{+}; $B = Mn^{4+}$, Fe^{3+}, Mn^{2+} (small and medium-sized ions); $X = O^{2-}$ and OH^{-}. Mathieson and Wadsley (1950) suggest the formula KMn_8O_{16} for cryptomelane.

Fleischer and Richmond (1942, 1945) report cryptomelane from Sitapur, but this is the first occurrence of cryptomelane to be recognized in the manganese ores of Mysore.

The above observation was made during a detailed study of the ore minerals of Indian manganese deposits, which study is still in progress. The work was carried on at the Laboratory of Economic Geology, Yale University. I am very grateful to Prof. Alan M. Bateman and Prof. Horace Winchell for their valuable direction and help.

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[1] Hardness determined by using an effect similar to the Becke ray used in petrography, suggested by Van der Veen, R. W., 1925, Mineragraphy and Ore Deposits, 28, The Hague.

Childrenite from the Lake District, Cumberland.

An erroneous record of the occurrence of childrenite in Cumberland has been included in some of the mineralogical literature, as the result of a mis-statement in C. F. Rammelsberg's investigation of this mineral in 1852.[1] In this he refers to a locality 'near Callington in *Cumberland*', a mistake which seems to have passed unnoticed and become perpetuated in a shortened reference simply to 'Cumberland'. Callington is in Cornwall, and Rammelsberg's reference was almost certainly to the well-known locality of the George and Charlotte Mine, Tavistock, actually in Devon, but also *near* Callington, just over the county boundary.

We are, however, able to record a new and definite occurrence of childrenite in the Lake District in Cumberland. It was found in an unusual quartz-chlorite vein a little to the west of Causey Pike; this vein contains considerable amounts of apatite (in crystals up to an inch and more in length) and arsenopyrite, together with a little löllingite and scheelite, and is clearly of a lower-zone, higher-temperature type, with granitic affinities. Apart from this being a new locality for all of these five minerals, the position and presence here of this vein is very suggestive of and, in fact, provides strong evidence for the recent postulation by W. C. C. Rose,[2] from the occurrence of a well-defined thermal-metamorphic aureole surrounding it, of a steep-sided, stock-like (granitic) intrusion under Causey Pike.

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[1] Ann. Phys. Chem. (Poggendorff), vol. 85, p. 435.

[2] Proc. Geol. Assoc., 1954–5, vol. 65, pp. 402–406.

A new occurrence of nadorite in Cornwall.

In 1927 Sir Arthur Russell[1] recorded the finding by himself in 1907 of a single specimen of nadorite, for the first time in the British Isles, at the Bodannon mine, St. Endellion, Cornwall, describing, as well, a second specimen collected (but not apparently identified) at the same mine in 1919 by Prof. A. Hutchinson, of Cambridge, whose attention it had attracted.

These appear to have been the only two specimens of this rare mineral so far found and recorded in Britain, but I have since identified two further specimens, collected by myself in the same area in 1938.

One of these is from a new locality, Trevinnick Mine, St. Kew, and shows small, stout tabular crystals of nadorite, of a dark reddish-brown colour, with bindheimite, senarmontite, valentinite (and probably anglesite) in two cavities in compact, massive jamesonite; these crystals are of much the same habit as those on the Hutchinson specimen (No. 2) described by Sir Arthur.

The second specimen, from Bodannon Mine, shows minute, dark-brown short-prismatic crystals of nadorite, with anglesite and octahedra of senarmontite, in a small cavity in massive, fibrous jamesonite; these crystals are different in habit from those on all the other three specimens and resemble more those figured by Dana[2] from Djebel Nador, Algeria.

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[1] Min. Mag. 1927, vol. 21, p. 272.
[2] System of Mineralogy, 6th edn., 1892, p. 863, fig. 1.

New occurrences of arseniosiderite.

Several new occurrences of arseniosiderite (basic arsenate of calcium and iron) have recently been confirmed, for the first time in Britain: so far we have found it at four localities in Cumberland, one in Cornwall, and one in Devon. The Cumberland localities are: Grains Gill, Carrock Fell, where it occurs in drusy, slightly botryoidal aggregates of minute, brown, glistening scales coating quartz and arsenopyrite; higher part of Brandy Gill, Carrock Fell, in the outcrop of the east–west lead–copper vein, where it forms similar crusts of minute brown scales, and fibrous aggregates; at both these localities it is probably derived from alteration of scorodite; in the oxidized near-outcrop of a roughly N.W.–S.E. vein,

which in depth carries arsenopyrite, blende, and galena, between Sandbed and Potts Gill (baryte) Mines, near Caldbeck; here it forms tufts of minute, brown, glistening scales and is associated with scorodite, beudantite, and carminite; in material from a vein in Ingray Gill, near Caldbeck, where it is associated with pharmacosiderite, scorodite, and erythrite; here it is almost certainly derived from alteration of the erythrite. Apart from its occurrence in the Paddy End section of Coniston Mines, this is the only definite erythrite that we have so far confirmed in the Lake District; its reported occurrence at 'Force Crag' and at the nearby so-called 'Cobalt Mine', in the Causey Pike range (both of which probably refer to the same, latter, locality), is of considerable doubt. X-ray examination of many specimens of pink minerals collected at the so-called 'Cobalt Mine', and which, superficially, might be taken for erythrite, has in almost every case shown them to be scorodite; the other examples of this material are simply iron-stained, altered apatite.

In Cornwall arseniosiderite has been found at Penberthy Croft Mine, St. Hilary, associated with scorodite and decomposed arsenopyrite, and in Devon, at Huckworthy Bridge Mine, Sampford Spiney, associated with, and probably derived from alteration of, erythrite.

The mineral may be commoner than supposed as it is easily overlooked. X-ray powder photographs are identical with each other and with that of arseniosiderite from the original locality at Romanèche, Saône-et-Loire, France.

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New occurrences of phosgenite.

PHOSGENITE, lead chlorocarbonate, has so far only been known to occur with certainty at two British localities, namely the Bage Mine, Bole Hill, near Wirksworth, Derbyshire (= the various localities usually given in the literature and on labels with old specimens as 'Cromford' or 'Matlock'), and Wheal Rose, Sithney, Cornwall, whence it was described in 1927 by Sir Arthur Russell,[1] who also showed that other Cornish specimens, supposedly from Wheal Confidence, Newquay, undoubtedly came from Wheal Rose as well. No further specimens of the mineral had been found in Britain for a very long time.

Within the last few years I have discovered another locality in Cornwall, Penberthy Croft Mine, St. Hilary, where in a cavity in some decomposed, 'gossany' quartz–galena veinstone I found two small but well-defined prismatic crystals of phosgenite, associated with anglesite, on decomposed galena. The crystals of phosgenite are pale wine-yellow in colour, and of long prismatic habit, the larger of the two being about 8 mm. long and 2 mm. thick: both show well-developed terminal faces of *c*(001) and several small faces in the pyramid and prism zones, but the latter are in general very striated, with many small vicinal faces, and owing to the positions of the crystals in the cavity it is difficult to make out what most of the faces are.

A second occurrence has also been identified, in Cumberland, from the outcrop of the main Driggith–Sandbed vein near Caldbeck, in an old opencast between the two mines: here colourless phosgenite has been found with anglesite in somewhat decomposed, massive granular galena.

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[1] Min. Mag., 1927, vol. 21, p. 221.

New occurrences of rosasite in Britain.

ROSASITE, $(Cu,Zn)_2CO_3(OH)_2$, was first described from the Rosas Mine, Sulcis, Sardinia, and has since been recorded from several localities in the U.S.A., at Tsumeb in South-West Africa, and in northern Turkestan. It is probably the zinc-rich end member, with Cu:Zn near 3:2, of an isostructural series with malachite, the X-ray powder-patterns being similar but with different spacings and quite distinct. It is possible that the series is continued farther in the zinc-rich direction, towards aurichalcite, $(Zn,Cu)_5(CO_3)_2(OH)_6$, but that with Zn becoming predominant over Cu there is a change of lattice to orthorhombic.

Though a likely mineral to be found at several localities, rosasite has not so far been reported in Britain, but we are now able to record no less than seven occurrences. In the Lake District, at Driggith Mine, Caldbeck (12- and 30-fathom levels); Sandbed Mine, Caldbeck (Upper level); Roughtongill Mine (outcrop of the south vein and 60-fathom level); Silvergill Mine (Middle level, on north vein); a copper vein near Potts Gill, Caldbeck; Tongue, or Ruthwaite Lodge, vein, Grisedale Mines, Patterdale; at all these localities the rosasite generally forms small bluish-green wart-like aggregates, though the colour may vary from

malachite-green to pale blue, its usual associates being smithsonite hemimorphite, malachite, aurichalcite, and the ill-defined zinc-bearin varieties of malachite referable to 'paraurichalcite' or 'cuprozincite which are very similar. In Cornwall, one of us (A. W. G. K.) has foun rosasite at Penberthy Croft Mine, St. Hilary, associated with malachit and native silver in a much decomposed veinstone.

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Carpholite from Cumberland and Cornwall.

THE rare manganese aluminium silicate, carpholite, hitherto onl recorded from a few foreign localities, has been recently found by us i Cumberland and in Cornwall.

In Grains Gill, Carrock Fell, in the northern Lake District, carpholi occurs in thin, fibrous-radiating aggregates in joints in white vein-quart specimens collected being derived almost certainly from the Emerso vein of the Carrock Wolfram Mine. In contrast to its more usual dee straw- or wax-yellow colour, the Grains Gill mineral is of a pale, almo cream yellow, and until the quartz is broken appears merely as a fai yellowish staining.

Carpholite, again pale in colour, has also been found by one of us three localities in Cornwall: in an old opencast on Kit Hill, and (a slightly greenish colour) in material from the south workings Hingston Down Consols Mine, both these localities being near Callingto and at Stennagwynn Mine, St. Stephen-in-Brannel; at the two form it occurs in joints in greisen, while at Stennagwynn it also coats joints altered granite and closely resembles wavellite, for which this mine one of the few known Cornish localities.

X-ray powder-photographs are all in agreement with that of carpho ite from Schlaggenwald, Bohemia.

At all the above-mentioned new localities the carpholite occurs association with wolfram.

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